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SOIL SCIENCE

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Contents

Joseph N. Harper, 1874–1936 241
Properties of the Hydroxyl Groups of Clay as a Basis for Characterizing a Mineral Soil. WALTER THOMAS 243
The Applicability of Alkaline Permanganate for Oxidation of Organic Matter in Soils for Mechanical Analysis. JOGENDRA NATH CHAKRABORTY 261
Dispersion of Soil for Mechanical Analysis by Sodium Carbonate or Sodium Oxalate Treatment. AMAR NATH PURI 267
Behavior of Polyvalent Cations in Base Exchange. J. E. GIESEKING AND HANS JENNY 273
The Effect of Phosphates on the Cation Exchange Capacity of Certain Soils. A. L. PRINCE AND S. J. TOTH 281
Availability of Soil Phosphates for the Plant from the Viewpoint of Colloid Chemistry. A. TH. TIULIN 291
Physiological Studies on Rhizobium: VII. Some Physiological Effects of Accessory Growth Factors. D. W. THORNE AND R. H. WALKER 301
Book Reviews 311

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JOSEPH N. HARPER

Joseph N. Harper
1874-1936

Dr. Joseph N. Harper, for many years identified and widely known in connection with soil fertility interests in the South, passed away at his home at Atlanta, Georgia, July 1. His many friends who have known of his poor health due to a heart ailment, nevertheless were sadly shocked, since he had been active up to within a few days of his death.

Few agriculturists in the South have been more closely allied with its soil fertility problems than was Joseph Harper. Born March 11, 1874, and reared on a farm in Winston County, Mississippi, he began his advisory career with his appointment in 1898 as agronomist to the Kentucky Agricultural Experiment Station where he made notable contributions on the culture of tobacco, corn, wheat, and hemp.

In 1904 he installed at the St. Louis fair a Kentucky agricultural exhibit which won a grand prize and many medals and led to a special invitation from the Department of Agricultural Technology of Ireland to visit that country and conduct experiments with tobacco. While abroad, Doctor Harper studied soils and methods practiced by farmers in maintaining soil fertility in the British Isles.

In 1905 he was called to head the department of agriculture of Clemson College, South Carolina, and to direct the activities of the South Carolina Experiment Station. These positions he held for 11 years, and under his direction the research department of Clemson College grew until it became recognized as a leading experiment station dealing with problems of soil fertility and plant diseases.

Doctor Harper, in 1917, was chosen to direct the extensive work of the Soil Improvement Committee of the Southern Fertilizer Association. His sound scientific knowledge and practical judgment won for him, in his travels all over the South, the respect of all concerned with the maintenance and building up of soil fertility.

After a year as director of the department of crop fertilization of W. R. Grace & Co., in 1925 Doctor Harper accepted a position as director of agricultural research for the Société Commerciale des Potasses d'Alsace with headquarters in Atlanta. With the formation of N. V. Potash Export My., Inc., Doctor Harper became a director of this company's agricultural and scientific bureau, in charge of the southern territory, which position he held until the formation of the American Potash Institute, Inc., in July, 1935. For the institute he was manager of the southern territory.

Doctor Harper held memberships in many scientific societies and had held every office in the Association of Agricultural Workers, which is composed of the leading agricultural scientists of the South. It has been said of him that his success was due not only to his scientific knowledge, but to his practical knowledge of farming, and that when he talked to farmers he had his own experience of a lifetime of farming from which to draw.

He is survived by Mrs. Harper, whom as Miss Susan Sparks he married in 1898, and by one daughter, Lucy Elizabeth.

R. H. STINCHFIELD.

PROPERTIES OF THE HYDROXYL GROUPS OF CLAY AS A BASIS FOR CHARACTERIZING A MINERAL SOIL[1]

WALTER THOMAS

Pennsylvania State College

Received for publication June 20, 1936

INTRODUCTION

By the conductometric titration of a soil treated with increasing concentrations of $Ba(OH)_2$, Hissink (17, 18) found that the salt line representing the formation of the barium salt of the soil acids coincided with the abscissa on which were plotted the quantities of $Ba(OH)_2$ added, indicating saturation of these acid functions. It has been found also by Hissink and later by others that the conductivity of the solution at the points of the straight portion of the baryta line is proportional to the content of baryta in solution. Hissink accordingly proposed that the degree of unsaturation of a soil represented by his quantity $T - S$ (T = maximum absorbing capacity, S = replaceable bases) could be determined by the point represented by the intersection of the straight portion of the baryta line with the abscissa. Hissink pointed out that, although the method was not free of objection, the horizontal portion of the bartya line corresponded approximately to the so-called "replaceable" hydrogen ions. But a number of investigators (2, 20, 21, 24, 26) have pointed out that Hissink's quantity ($T - S$) is much higher than that corresponding to the replaceable hydrogen ions.

The resulting confusion appears to have delayed the recognition of the possibilities of the acid and base titrametric method as a means for the rapid characterization of soils. The principal objection which has been raised is that secondary reactions take place—that the barium (or calcium) hydroxide reacts not only with the base exchange components but also with other constituents of the soil—when *an excess* of alkali or alkali hydroxides is added to a soil (21, 25).

On the other hand, by treating soils with increasing concentrations (0.005 N to 0.04 N per gram of soil) of $Ba(OH)_2$ in aqueous solution and also of KOH in alcoholic solution both before and after leaching with a solution of 0.05 N HCl, Clarens (12) has *established the existence of a gamut of acidic functions in a soil, the barium salts of one of which are decomposed by carbonic acid but not by water.* The existence of such unsaturated functions was established even in soils containing as high as 6.6 per cent $CaCO_3$. From these experiments

[1] Authorized for publication on June 18, 1936, as Paper No. 733 in the Journal Series of the Pennsylvania Agricultural Experiment Station.

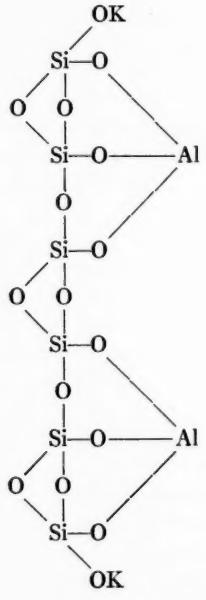
Clarens (5, 6, 9, 11, 12, 13) developed a method for the rapid characterization of a soil which the writer made use of on being confronted with difficulties in the interpretation of some of the results obtained in investigations on the condition of the phosphorus and also of the potassium in apple tree cylinder experiments (28, 31) by methods of continuous extraction with different dilute acids (30, 31).

The concept developed is essentially one that is at present generally accepted; namely, that the dominant exchange complex in soils of mineral origin consists of a series of alumino-silicic acids containing hydrogen ions of different activities (reaction values) (1, 3, 15, 24).

The constitution of the feldspars, kaolins, and clays

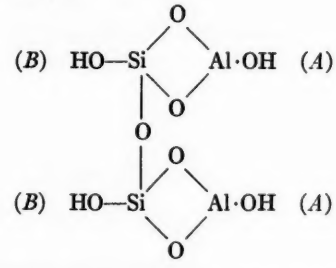
The constitutional formulas of the feldspars, kaolins, and clays represented below are not given as final but as indicating the convergence of our present knowledge. They serve as a means to the interpretation of the results of our experiments.

Basing our concepts of the constitution of the silicates of aluminum given by Clarke (14), we may deduce the structural formula of an unmixed orthoclase feldspar ($K_2Al_2Si_6O_{16}$)



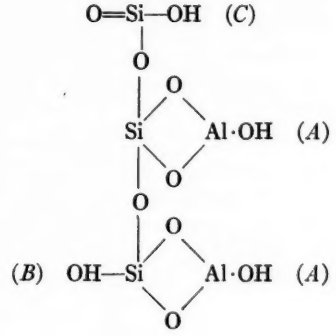
from one of the ortho-silicic acids (H_4SiO_4), by the elimination of 8 molecules of water from 6 molecules of H_4SiO_4 and the substitution of 6 hydrogen by 2

aluminum atoms and 2 hydrogen by 2 potassium atoms; and the constitution of a pure kaolin ($H_4Al_2Si_2O_9$)

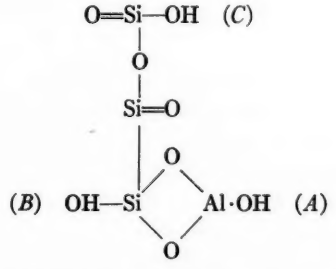


from orthoclase feldspar by the elimination of 4 molecules of SiO_2 and 2 of K.

In accordance with current concepts of the constitution of clay; namely, that clays are compounds of a series of alumino-silicic acids and feldspars, we may then deduce the structural formula for clay as typified by the following constitutional formulas:



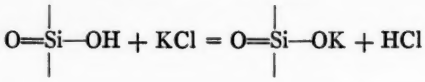
or (9)



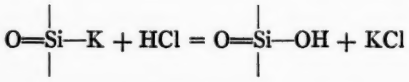
The three types of hydroxyl groups of clays

It is to be noted that the hydroxyl groups marked (*C*) in the formula for clay are not present in kaolin. Experimental evidence in support of this will

be given later. Since these OH groups denoted by (*C*) are attached directly to Si atoms not directly linked to the Al atoms, they will possess distinct acidic properties—functioning as hydrogen silicate—and can be replaced partially or wholly by different metals, such as K, Ca, Mg.



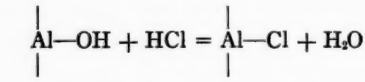
and, conversely,



Some of these hydroxyl groups marked (*C*) are free, and a portion of them may be replaced by bases. The free hydrogens can be determined by the quantity of $Ba(OH)_2$ *neutralized* in the formation of barium salts; and the hydrogens replaced by metals, by the quantity of HCl required to effect this substitution.

The hydroxyl groups marked (*B*) are linked to the Si atoms connected to Al atoms by an oxygen linkage. The hydrogens of these groups marked (*B*), therefore, will possess less pronounced acidic properties than those marked (*C*). With baryta the neutralization of the hydrogens of the OH groups marked (*B*) is only partial, since (*vide infra*) the barium salts of these acidic functions are hydrolyzed by water.

The hydroxyl groups denoted by (*A*) are linked directly to Al, an electropositive element with basic properties. The salts obtained by the substitution of acid radicals in these OH groups undergo partial hydrolysis. The total replacement of these hydroxyl groups marked (*A*) can be obtained only when an excess of acid is used. When treated with an acid the amount of the acid radical fixed serves to evaluate the number of these hydroxyl groups substituted (*vide infra*)



MATERIALS AND METHODS

The original soil and also soils from two of the metal cylinders were used in these experiments. The soil designated as the "original" soil is the soil in its initial state before being introduced into the cylinders. It is a virgin soil of the Hagerstown series and has been fully described in an earlier publication (27). The soils designated "NPK" and "check" are representative of the samples of soils taken at the end of the experiment in the manner already described (29) from the surface 0–7 inches of the NPK treated and untreated cylinders under cultivation.

To 1-gm. portions of soil (sieved to pass a 100-mesh screen) in two series of tubes (from eight to ten tubes in each series) were added, to the one series,

increasing quantities of 0.1 *N* HCl and, to the other, increasing amounts of 0.1 *N* $Ba(OH)_2$ in the following manner: To one tube 19 cc. of water and 1 cc. 0.1 *N* HCl (or 0.1 *N* $Ba(OH)_2$), to a second 18 cc. of water and 2 cc. of 0.1 *N* HCl (or 0.1 *N* $Ba(OH)_2$), and so on for eight to ten tubes. The volume of the solution in each tube is accordingly 20 cc. Freshly boiled distilled water was

TABLE 1

Amounts of 0.1 N HCl and of 0.1 N $Ba(OH)_2$ remaining in solution after treatment of the "original" soil with increasing amounts of the acid and base

cc. 0.1 *N* HCl			cc. 0.1 *N* $Ba(OH)_2$		
Added	Remaining in solution	Fixed	Added	Remaining in solution	Fixed
1	0.20	0.80	1	0	1.00
2	1.05	0.95	2	0.30	1.65
3	1.90	1.10	3	1.10	1.90
4	2.75	1.25	4	1.90	2.10
5	3.60	1.40	5	2.70	2.30
6	4.55	1.45	6	3.65	2.35
7	5.55	1.45	7	4.65	2.35
8	6.55	1.45	8	5.65	2.35
9	7.40	1.60	9	6.50	2.50
10	8.30	1.70	10	7.35	2.65

TABLE 2

Amounts of 0.1 N HCl and of 0.1 N $Ba(OH)_2$ remaining in solution after treatment of the check soil with increasing amounts of the acid and base

cc. 0.1 *N* HCl			cc. 0.1 *N* $Ba(OH)_2$		
Added	Remaining in solution	Fixed	Added	Remaining in solution	Fixed
1	0.15	0.90	1	0	1.00
2	0.85	1.20	2	0.25	1.75
3	1.55	1.45	3	1.05	1.95
4	2.50	1.50	4	1.90	2.10
5	3.45	1.55	5	2.80	2.20
6	4.35	1.65	6	3.75	2.25
7	5.35	1.65	7	4.75	2.25
8	6.10	1.90	8	5.60	2.40
9	6.95	2.05	9	6.35	2.65
10	7.80	2.20	10	7.15	2.85

used. After leaving the soil in contact with the reagent for 18 hours, the tubes were continuously shaken for 6 hours. On settling, the solutions were filtered with suction with proper precautions in the case of $Ba(OH)_2$, and the number of cubic centimeters of 0.1 *N* HCl remaining in an aliquot (10 cc.) was titrated with methyl orange as indicator against standard alkali. The 0.1 *N* $Ba(OH)_2$

remaining in solution was titrated with phenolphthalein as indicator against standard acid.

For reasons the significance of which is pointed out later in this paper, the

TABLE 3

Amounts of 0.1 N HCl and of 0.1 N $Ba(OH)_2$ remaining in solution after treatment of the NPK soil with increasing amounts of the acid and base

cc. 0.1 *N* HCl			cc. 0.1 *N* $Ba(OH)_2$		
Added	Remaining in solution	Fixed	Added	Remaining in solution	Fixed
1	0.10	0.90	1	0	1.00
2	0.70	1.30	2	0.20	1.80
3	1.30	1.70	3	0.95	2.05
4	2.20	1.80	4	1.65	2.35
5	3.10	1.90	5	2.45	2.55
6	3.95	2.05	6	3.35	2.65
7	4.85	2.15	7	4.35	2.65
8	5.65	2.35	8	5.35	2.65
9	6.45	2.55	9	6.25	2.75
10	7.20	2.70	10	7.15	2.85

TABLE 4

Amounts of 0.1 N NaOH required to satisfy all bases remaining in solution, including Al and Fe, after treatment of the soils with increasing amounts of 0.1 N HCl

(Phenolphthalein titration of boiling solutions following the titration with methyl orange)

ORIGINAL		CHECK		NPK	
0.1 *N* HCl added	0.1 *N* NaOH required to neutralize all bases remaining in solution	0.1 *N* HCl added	0.1 *N* NaOH required to neutralize all bases remaining in solution	0.1 *N* HCl added	0.1 *N* NaOH required to neutralize all bases remaining in solution
cc.	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*
1	0.50	1	0.50	1	0.50
2	1.50	2	1.40	2	1.30
3	2.45	3	2.30	3	2.15
4	3.50	4	3.30	4	3.15
5	4.50	5	4.40	5	4.10
6	5.55	6	5.45	6	5.10
7	6.60	7	6.55	7	6.10
8	7.60	8	7.55	8	7.10
9	8.45	9	8.40	9	8.00
10	9.35	10	9.30	10	8.90

titration of the HCl remaining in solution is made first with methyl orange in the cold. The solution is then heated to boiling, and after the addition of a few drops of phenolphthalein the titration is continued to a permanent pink color.

EXPERIMENTAL DATA

The results are given in tables 1 to 4 and are shown graphically in figures 1 to 3.

The "neutralization" portion of the graphs obtained for a particular soil consists of three segments; the equilibrium points making up each of the segments lie approximately on a straight line, the deviations being relatively small. The first segment is horizontal and, therefore, coincides with the abscissa; a

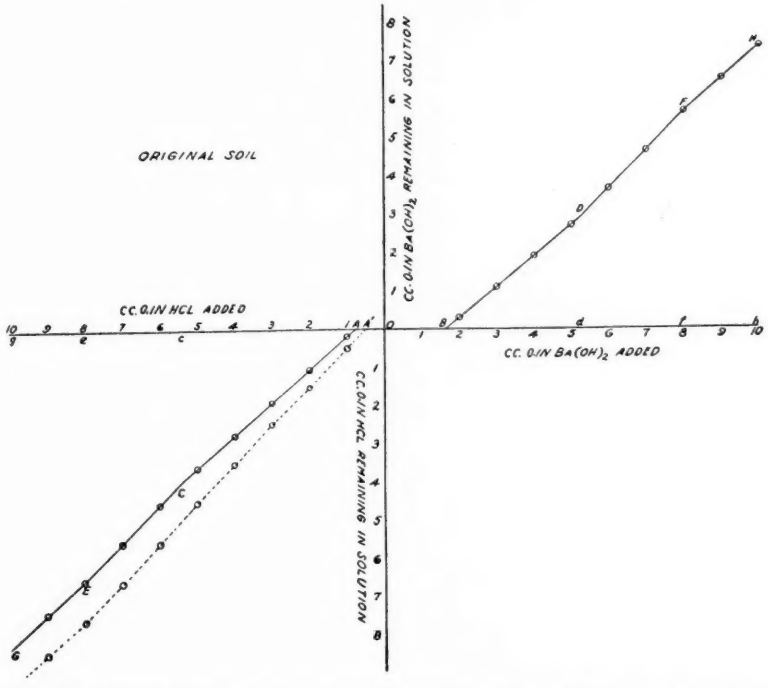


FIG. 1. THE "ORIGINAL" SOIL TREATED WITH SOLUTIONS OF 0.1 *N* HCl AND OF 0.1 *N* $Ba(OH)_2$

second segment makes an angle of less than 45°; and a third segment has an angle the tangent of which is approximately unity, indicating saturation at the higher concentrations.

DISCUSSION OF RESULTS

The interpretation of the graphs

The results for the "original" soil, represented in figure 1, are described in detail to illustrate the method of interpretation.

The segment OB. In the "original" soil OB is equal to 1.62. This indicates that complete fixation of the baryta added has occurred up to a concentration of 1.62 cc. 0.1 *N* $Ba(OH)_2$ per gram of soil. The segment OB then evaluates those acidic functions the barium salts of which are not hydrolyzed by water free from CO_2 and corresponds to the unsaturated part of the hydroxyl groups denoted by (*C*) in the formula for clay previously given. Even in soils containing large amounts of $CaCO_3$, the segment OB will not be zero because

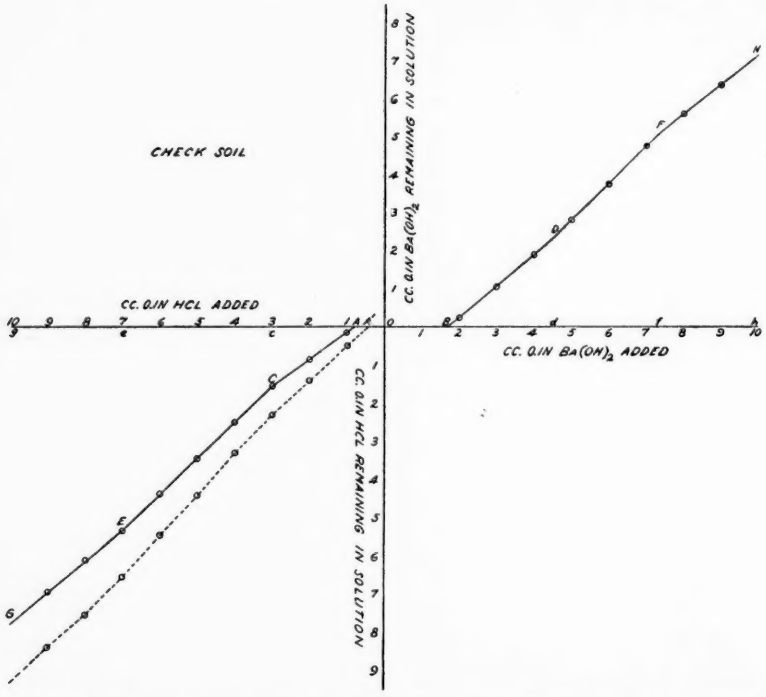


FIG. 2. THE "CHECK" SOIL TREATED WITH SOLUTIONS OF 0.1 *N* HCl AND OF 0.1 *N* $Ba(OH)_2$

of the presence of $Ca(HCO_3)_2$ in the soil solution. OB is only fully saturated by $Ba(OH)_2$ or, therefore, by $Ca(OH)_2$ when a slight excess of alkali is present.

The segment BD. After the replacement (neutralization) of the hydrogens represented by the segment OB, there still exist acidic functions the barium salts of which are partially hydrolyzed by water. This segment BD corresponds to those hydroxyl groups marked (*B*) and makes an angle—tan $D_Bd = 0.82$. This indicates that after a quantity of 0.1 *N* $Ba(OH)_2$ equal to OB (1.62 cc. per gram of soil) is added, the fixation of this base is only 18 per cent. The segment BD is evaluated thus: Bd − Dd = 3.40 − 2.70 =

0.70 cc. 0.1 *N* $Ba(OH)_2$ per gram of soil. The point d represents the intersection of the perpendicular from D to the abscissa. The acid functions represented by BD are of no practical importance, since the complete saturation of these groups would necessitate such an excess of base as would make the soil unfit for plants to thrive.

The segment DF. Commencing at D the third segment, DF, makes an angle of approximately 45° with the abscissa, indicating that the fixation of the base along this segment is nil, with formation of barium salts corresponding to other

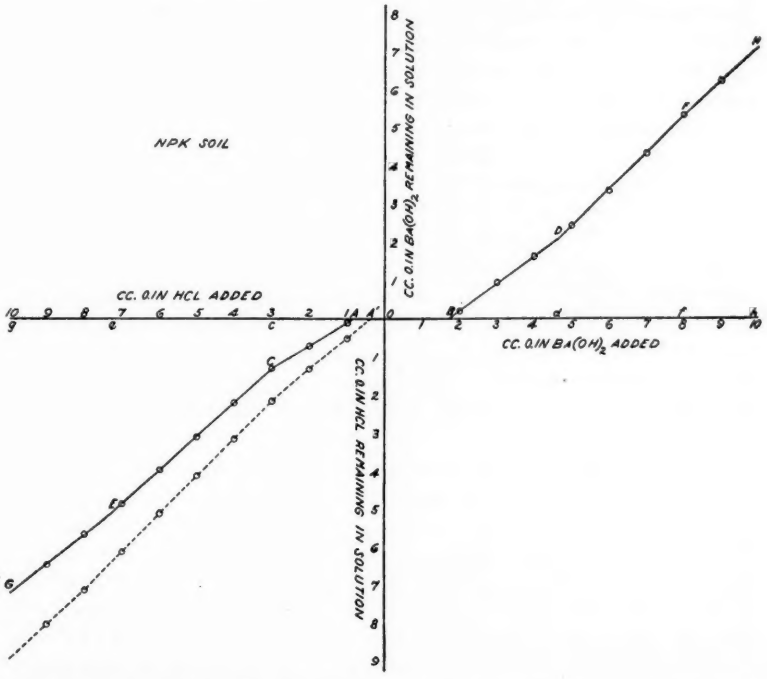


FIG. 3. THE "NPK" SOIL TREATED WITH SOLUTIONS OF 0.1 *N* HCl AND OF 0.1 *N* $Ba(OH)_2$

acidic functions having no affinity for $Ba(OH)_2$. Above a concentration of 8 cc. 0.1 *N* $Ba(OH)_2$ the curve again breaks and makes with the abscissa an angle the tangent of which is less than that made by DF. This segment FH has no bearing in these experiments. It is an indication of the instability of the clay complex, since above this concentration the baryta, instead of neutralizing, reacted with some of the components of the clay.

The segment OA. In the "original" soil OA is equal to 0.76 cc. In the absence of free bases, such as $Al(OH)_3$, $Fe(OH)_3$, $CaCO_3$, this segment would represent the number of cubic centimeters of 0.1 *N* HCl per gram of soil re-

quired to react with the exchangeable bases. OA then represents that fraction of the hydroxyl groups marked (*C*) the hydrogens of which have been replaced by metals.

If kaolin is substituted for soil in these experiments the points O, A, and B almost coincide (9). Even when digested with 1.7 *N* HCl for 10 hours in a boiling water bath, no decrease in the exchange capacity of either dickite or kaolin occurred (15). The segment AB, therefore, is relatively insignificant in kaolin, evidence that the hydroxyl groups marked (*C*) have, therefore, no equivalent in kaolin. The remainder of the graphs for kaolin do not differ from that for soils, i.e., there is a segment AC making an angle of less than 45° and a third segment the tangent of which is unity.

Although in the case of most of the soils examined by Clarens, free aluminum and iron hydroxides were absent, this is not the case with the Hagerstown soils reported here. The behavior of this Hagerstown clay loam to very low concentrations of HCl (0.000182 *M* to 0.00182 *M*) is intermediate to the behavior of kaolin and that of feldspar.

Whereas in kaolin the segment OA is insignificant, in feldspars the whole of this segment OA is represented by Al (9). An unmixed feldspar, examined by the writer, treated with increasing quantities of 0.1 *N* HCl titrated against 0.1 *N* alkali, using as indicators methyl orange followed by phenolphthalein, as described, subsequently, gave OA = 2.6 cc. 0.1 *N* NaOH per gram of feldspar and OA′ = 0.05. AA′, therefore, is equal to 2.55, showing that practically all of the exchangeable bases in this feldspar are represented by Al. The segment OB for feldspar was found to be 0.15 and, therefore, practically negligible.

It is evident then that the segment OA represents the exchangeable bases only if the soil contains no free bases or carbonates that may react with the acid employed. In the soils reported here the carbonates are relatively low (0.05 per cent), but appreciable quantities of "free" aluminum (and iron) are present. The fraction of the segment OA to be assigned to Al_2O_3 and Fe_2O_3 is represented in the figures by AA′ and can be obtained by titration with 0.1 *N* NaOH first at room temperature with methyl orange as indicator followed by titration of the solution raised to boiling temperature using phenolphthalein as indicator. A solution of $AlCl_3$ (or $FeCl_6$) neutral to methyl orange is acid to phenolphthalein. In titrating with 0.1 *N* NaOH starting from the point of neutralization with methyl orange, the phenolphthalein turns color only when all the aluminum and iron are precipitated as hydroxides. The difference between the two titration values with these indicators gives approximately, therefore, the quantity of $Al(OH_3)$ (and $Fe(OH)_3$) in solution in the form of $AlCl_3$ (or $FeCl_3$). The broken lines (fig. 1–3) and table 4 give the results with phenolphthalein as indicator.

In the "original" soil AA′ = 0.26 cc. gives the Al (and Fe) replaced per gram of soil. The exchangeable bases are represented by OA′ = 0.50 cc. 0.1 *N* HCl per gram of soil. In order to determine OA in calcareous soils, it is neces-

sary to ascertain the quantity of 0.1 *N* acid necessary to neutralize the calcium carbonate in 1 gm. of soil. This quantity is then subtracted from the value obtained for the segment OA.

The segment AC. In the "original" soil the second segment AC makes an angle tan cAC = 0.84, indicating that the HCl has been fixed to the extent of 16 per cent. The value of AC is given by Ac − Cc = 0.7 cc. 0.1 *N* HCl per gram of soil, where c is the perpendicular from C on to the abscissa.

The acidic functions represented by the segment AC cannot be replaced by $Ba(OH)_2$. This has been repeatedly established (9) by treatment of soils which have previously been treated with increasing quantities of 0.1 *N* HCl in the manner already indicated, with increasing quantities of 0.1 *N* $Ba(OH)_2$ in amounts more than sufficient to effect complete substitution of all the hydrogen atoms. In all cases the hydrogen replaced by barium was always expressed by the value of the segment AB before the initial treatment with HCl. The segment AC then must correspond to the hydroxyl groups marked (*A*) in direct attachment with Al. Relative to the origin of the aluminum, Clarens states (10)[2]:

> This aluminum could have prevously existed in the free state or even have come from new silicates, which may either have remained attached to the rest of the molecule, so that spaces left by the aluminum might be filled by a metal of some sort, or have been carried off themselves in the form of SiO_2. The importance of these alternatives to the fate of feldspar that has become clay, or more accurately zeolite, is apparent.
>
> . . . It is evident that the feldspar which we have just been studying will not be transformed into zeolitic clay by the usual means (replacement of the alkaline and alkaline earth bases by various agents, particularly by H_2CO_3). It is the aluminum which will first be replaced, according to circumstances, by various bases which, in the resulting zeolitic clay, will constitute the replaceable bases; a small, usually very small, amount of the aluminum may perhaps remain and also act as a replaceable base. It is the potassium thus fixed that is called the "assimilable" potassium of the clay.

The segment CE. A third segment, CE, making an angle of 45° indicates that the acid functions represented are saturated and that no further fixation takes place.

On the addition of more acid the curve again breaks and makes an angle of less than 45°. Inasmuch as this indicates an attack on the clay nucleus, it is of no interest in these experiments.

The three segments of importance in application. The most important segments are OA, OB, and AC. OA evaluates, in the absence of free aluminum and ferric hydroxides and calcium carbonate, the acidic functions actually saturated by the so-called "replaceable bases"; OB evaluates free acidic functions the barium salts of which are not hydrolyzed by water free from CO_2 in the presence of a slight excess of base. The segment AC bears the same relation to acids, in particular to phosphoric acid, as the segment BD does to bases. This fact may be used to determine the amount of phosphoric acid

[2] Translation from the original French.

necessary to satisfy the Al and Fe. It should be apparent that only four points are required to obtain all three segments.

Application to the determination of the amount of phosphoric acid required to satisfy the Al and Fe

In the "original" soil the angle which AC makes with the abscissa (tan = 0.84) indicates (assuming the fertilizer to be mixed thoroughly with the soil, which is never the case in practice) that if less than 0.84 cc. 0.1 *N* phosphoric acid per gram of soil be added the whole of the phosphoric acid would be fixed, resulting in a low concentration of phosphorus in the soil solution until this "threshold value" is exceeded.

Calculated as P_2O_5, the threshold value for the "original" soil is equal to

$$0.84 \times 0.002358 \times 585130 = 1159 \text{ gm. } P_2O_5$$

where 0.002358 is the number of grams of P_2O_5 in 1 cc. of 0.1 *N* acid and 585130 is the weight of the soil (in grams) in the 0 to 7-inch layer. Eleven hundred and fifty-nine grams of P_2O_5 is then required to saturate the segment represented by AC of the 0 to 7-inch layer in the "original" soil. Calculated to an acre basis of 2,000,000 pounds the value obtained is 3957 pounds P_2O_5, which is relatively enormous. In practice, the phosphate fertilizer is not intimately mixed with the whole of the first 7 inches. Under field conditions the diffusion of phosphate is very slow and frequently extends over a long period, thus allowing portions of the soil to be in contact with high concentrations of phosphate, and for this fraction the limiting value above is passed.

Application to determine lime requirement of soils

Many authorities are of the belief that there has been no satisfactory laboratory method developed thus far that can with certainty be substituted for the field-trial method for the determination of the lime requirements of soils. There is, however, a sound theoretical basis for the determination of the lime requirement by the present method.

It has frequently been assumed that when $CaCO_3$ is added to an acid soil the chief chemical reaction is with the so-called "replaceable" hydrogen ions of the exchange complex, i.e., the hydrogen ions replaceable by the base of a neutral salt. From the viewpoint presented it would not be logical to expect any definite relationship between the replaceable hydrogens and the degree of unsaturation of the exchange complex. Consequently, the determination of the replaceable hydrogen would not be a measure of the lime requirements of soils. The neutralization of replaceable H is only one of the factors involved in liming. Nor would it be in accordance with the concepts presented, to use as a basis for the lime requirement a quantity of $CaCO_3$ corresponding to the segment OB, for—because of the presence of $Ca(HCO_3)_2$ in the soil solution (see discussion of the segment OB)—this segment could never become nil even in soils in which large amounts of $CaCO_3$ has persisted for many years. The

complete saturation of the segment OB can take place only in the presence of a slight excess of the hydroxide. It follows that the amount of $CaCO_3$ necessary for neutralization cannot be determined by shaking the soil with an excess of precipitated $CaCO_3$ and then determining the decrease in the segment OB. The saturation of the soil is very slow as a result of the low solubility of $CaCO_3$ even in the presence of small quantities of CO_2.

Clarens (8) has pointed out that if a soluble salt of calcium such as $CaSO_4$ or $CaCl_2$ be added also with the $CaCO_3$, the segment OB is markedly reduced and the reduction is independent within certain limits of the concentration (0.1 to 0.05 *N*) of the solution used. The reduction in the amount of OB then gives the quantity of $CaCO_3$ necessary for the effective saturation of the soil considered.

The experiments are conducted in the same manner as previously described. Five 1-gm. portions of soil are shaken up with 0.1 gm. of precipitated $CaCO_3$ and 20 cc. of a saturated solution of $CaSO_4$. The solutions are filtered with suction, and the soil is transferred to test tubes. To the first are added 19 cc. of water and 1 cc. 0.1 *N* $Ba(OH)_2$, to the second 18 cc. water and 2 cc. 0.1 *N* $Ba(OH)_2$, etc. The tubes are allowed to stand 18 hours, then shaken continuously for 6 hours, and then titrated in the usual manner against 0.1 *N* HCl and the new segment OB is determined. The "original" soil treated in this way gave OB = 1.10 as against 1.62 before treatment. Therefore, the saturation of the segment due to $CaCO_3 + CaSO_4$ is $1.62 - 1.10 = 0.52$ cc.

If the $CaCO_3$ is omitted and 20 cc. of a saturated solution of $CaSO_4$ only is used, the new segment OB is slightly greater than in the presence of $CaCO_3$ (0.59 as against 0.52). This shows that the $CaCO_3$ has caused a progression of 0 toward A of only 0.07. The conclusion must, therefore, be drawn that the saturation of the soil was due almost completely to the soluble salt of Ca, even when $CaCO_3$ is also present with the soluble salt (8).

This would explain why some investigators have found that when either $Ca(OH)_2$ or $CaCO_3$ is incorporated in one layer of soil (32) or applied as a top-dressing (16) the neutralizing effect is almost nil on the adjacent layers.

Application to determine the existence of different states of availability of the replaceable potassium

Of the many methods which have been proposed to determine the availability of soil potassium the determination of the replaceable form is the most rational and is the one generally favored. But it has already been shown (19) that broad generalizations based on the method are not possible. An additional limitation is imposed on the concept of the identification of the exchangeable potassium with the available potassium if the exchangeable potassium can possess different degrees of availability according to its position in the clay nucleus (7).

Reasoning *a priori* would lead one to expect that an exchangeable base such as potassium would not occupy the same position in the crystal lattice of the

clay nucleus; and within the past few years experimental evidence has been brought to support this premise (4, 22, 23). It would follow, therefore, that the replaceable potassium should exist in different degrees of availability to the plant. If this is the case then the processes of mobilization in which the soil potassium is rendered available would be discontinuous and would be reflected by broken solubility curves.

The "original" surface soil has been investigated from this point of view in the following manner: 200-gm. portions of the "original" air-dry soil contained in 1000-cc. shaking flasks were treated with increasing amounts of 0.1 *N* HCl. To the first flask were added 975 cc. of distilled water and 25 cc. 0.1 *N* HCl; to the second, 950 cc. water and 50 cc. 0.1 *N* HCl; to the third, 925 cc. of water and 75 cc. 0.1 *N* HCl; and to the fourth, 900 cc. of water and 100 cc. 0.1 *N* HCl. The soils were then left in contact for 18 hours and then shaken continuously for 6 hours. Potassium was determined in an aliquot.

As shown in table 4, the replaceable bases of this "original" soil are equivalent to 0.50 cc. 0.1 *N* HCl per gram of soil. The amounts of HCl added to the

TABLE 5

Quantities of potassium liberated from the original soil by treatment with dilute solutions of HCl sufficient to satisfy 25, 50, 75, and 100 per cent, respectively, of the replaceable bases

0.1 *N* HCl ADDED	AMOUNT K_2O DISSOLVED	0.1 *N* HCl EQUIVALENT
cc.	*p.p.m.**	*cc.*
25	40	1.69
50	42	1.79
75	95	2.00
100	87	1.89

* Dry soil.

flasks in this experiment accordingly were equivalent to one-fourth, one-half, three-fourths, and the whole of the replaceable bases, respectively. The results are given in table 5.

These results indicate that, within the range of concentration of HCl used, the solubility curve for the replaceable potassium is a discontinuous one.

Application to determine the changes produced by cultivation and fertilizer dressings

Although the aforementioned problems comprise the principal uses to which the method is adapted, it is of interest to ascertain what changes the method reveals in the properties of the initial condition of the soil at the end of the experimental period of 7 years. After introduction into the cylinders, both check and NPK soils were green manured each year with rye. The check soil received no mineral salts. The NPK soil received, during the whole experimental period of 7 years, total C. P. salt additions as follows: 465.5 gm. N, 1052.8 gm. P_2O_5, 1898 gm. K_2O—equivalent respectively to 1591 pounds N,

3598 pounds P_2O_5, 1898 pounds K_2O per acre 7 inches of 2,000,000 pounds. The precipitation during the whole experimental period was 260 inches, of which 96 inches fell during the experimental period in which the soil received mineral salts. All three soils are low in humus material. In spite of the green manuring, the humus material in the check and NPK soils was still relatively low, viz., <1.5 per cent.

The summarized results of the analytical data for the "original" soil and also for the check and NPK soils are given in table 6.

The divergences in the results of the check soil from the "original" soil are an indication of the joint effects of the growth of the trees and of the humus material from the green manures together with the climatic factors. The degree of unsaturation as represented by the segment OB has increased the equivalent of 0.06 cc. 0.1 *N* $Ba(OH)_2$ per gram of soil. The replaceable bases

TABLE 6

Comparative data for the original soil, the check, and NPK cylinders

SOIL	SEGMENT OA	SEGMENT OA′	SEGMENT AA′	SEGMENT OB	TAN < CAc	TAN < dBD
Original	0.76	0.50	0.26	1.62	0.84	0.82
Check	0.80	0.45	0.35	1.68	0.72	0.79
NPK	0.85	0.43	0.42	1.73	0.60	0.73

OA = Acid functions saturated by bases including free Fe and Al expressed in terms of cubic centimeters of 0.1 *N* HCl per gram of soil.

OA′ = Acid functions saturated by the so-called "replaceable bases" expressed in terms of cubic centimeters of 0.1 *N* HCl per gram of soil.

AA′ or OA − OA′ = "Free" $Al(OH)_3$ and $Fe(OH)_3$ expressed in terms of cubic centimeters of 0.1 *N* HCl per gram of soil.

OB = Unsaturated acidic functions the Ba salts of which are not hydrolyzed by water free from CO_2 in the presence of a slight excess of base. Expressed in terms of cubic centimeters of 0.1 *N* $Ba(OH)_2$ per gram of soil.

in the check soil have been reduced by the equivalent of 0.05 cc. 0.1 *N* HCl per gram of soil, whereas the "free" aluminum and iron have been increased by 0.09 cc. 0.1 *N* HCl per gram of soil. A decrease in the tangent of the angle CAc from 0.84 to 0.72 has occurred, which indicates an increment from a saturation of 16 per cent to a saturation of 28 per cent in the hydroxyl groups marked (*A*). The most rational explanation would appear to be that this increase is the result of the "deactivating" properties of humic acids (30).

The values for the NPK soil differ more widely from the corresponding values for the "original" soil than do those of the check soil. Particularly to be noted is the *increase* of the segment OB equivalent to 0.11 cc. 0.1 *N* $Ba(OH)_2$ per gram of soil; the *decrease* equivalent to 0.07 cc. 0.1 *N* HCl per gram of soil in the replaceable bases; and the relatively large increase equivalent to 0.16 cc. 0.1 *N* HCl per gram of soil in the "free" aluminum and iron hydroxides. The decrease in the tangent of the angle CAc is equivalent to 0.24, indicating

an increase of 24 per cent in the saturation of the hydroxyl groups marked (*A*) and representing the net effect of the deactivating properties of humic acids and the phosphate additions. In laboratory studies, Clarens (5) has reached the conclusion that salts of K, Na, NH_4, and Ca do not sensibly modify the unsaturated acid functions. The present experiment indicates that the resultant effect of the $NaNO_3$, K_2SO_4, and $CaH_4(PO_4)_2$ added as fertilizers upon the segments OA, AA′, and OB is similar in magnitude and direction to that produced by the green manuring alone. Moreover, it is a noteworthy fact that the salt additions have not caused any increase in the segment OA′ but, on the contrary, have diminished it slightly. It is the segment AA′ that has increased evidently at the expense of the so-called "replaceable bases."

SUMMARY

By the treatment of a soil with increasing amounts of solutions of hydrochloric acid and also of barium hydroxide in low concentrations, differences in specific properties of the three types of hydroxyl groups of clays may be used as a means for the rapid characterization of a soil with respect to the degree of unsaturation, the total replaceable bases, the "free" aluminum and iron hydroxides, the phosphoric acid required to satisfy the Al and Fe, the lime requirement, the availability of the different states of the replaceable potassium, and the changes produced by cultivation and fertilizer treatment.

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THE APPLICABILITY OF ALKALINE PERMANGANATE FOR OXIDATION OF ORGANIC MATTER IN SOILS FOR MECHANICAL ANALYSIS

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The successive developments and the present position of mechanical analysis of soils have been traced elsewhere (3). The International-A method was slightly modified in Versailles in 1934 according to the recommendation of Robinson (5), who advocates the use of 4 cc. *N* sodium hydroxide to 10 gm. soil and 500 cc. water instead of ammonia, which was previously prescribed for dispersion of soils. A similar conclusion was reached earlier by Chakraborty and Sen (2) while analyzing Indian lateritic soils. These soils refused to disperse fully unless they were shaken and converted into a suspension having a pH of about 10.5. For this purpose about 6–8 cc. *N* sodium hydroxide was required for 20 gm. of soil in 2 liters of water. Although Robinson's recommendations for the pretreatment of different types of soils for mechanical analysis appear to be superior to other proposals made so far, they are not altogether free from limitations. Hydrogen peroxide, which has been recommended for removal of organic matter, is a very costly and somewhat unstable reagent in tropical countries like India and it is catalytically decomposed by many soils. It has also been mentioned by Troell (6) that a fen soil with 37.7 per cent loss on ignition required more than 400 cc. of hydrogen peroxide used over 2 days for removal of organic matter. Similar difficulties have been encountered in the case of Indian soils having high loss on ignition. It is also to be remembered that any method which prescribes, as far as possible, the same mode of treatment for different types of soils in the course of mechanical analysis will be valuable because of the comparability of the results obtained by the particular method.

A new method (2) of dispersing soils involving the use of alkaline permanganate for oxidation of organic matter has been found successful in the case of Indian lateritic soils as shown by agreement of the results with those obtained by the International-A method. This method, which has been termed the "alkaline permanganate method," consists in oxidizing the soil organic matter

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TABLE 1

Oven-dry clay and clay + silt in air-dry soil by different methods

SOIL NO.	LAB. NO.	LOCALITY	INTERNATIONAL-A METHOD H_2O_2-HCl-NaOH (1 PER CENT SUSPENSION OF 20 GM. SOIL SHAKEN FOR 24 HOURS WITH 8 CC. *N* NaOH)			ALKALINE PERMANGANATE METHOD (1 PER CENT SUSPENSION OF 20 GM. SOIL SHAKEN FOR 6 HOURS WITH 8 CC. *N* NaOH)		
			Clay	Clay + silt	Loss on solution	Clay	Clay + silt	Loss on solution
			per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1	105	Bengal Dacca Bikrampur	21.2	62.3	1.5	21.2	62.6	1.8
		*Bengal soils**						
2	107	Rajshahi Farm	23.1	58.2	0.8	23.6	56.4	1.0
3	108	Berhampur Farm	19.8	47.1	0.9	20.1	47.5	1.0
4	109	Barisal	23.1	87.2	1.4	23.5	88.0	1.8
5	110	Jessore	17.2	38.1	0.9	18.6	40.2	1.0
6	111	Jalpaiguri Maynaguri Farm	9.1	44.8	1.2	9.3	45.5	1.4
7	112	Siliguri	5.5	14.0	1.5	5.5	13.6	1.4
8	113	Midnapore	20.5	47.8	0.7	20.5	47.3	0.6
		Bengal forest soils†						
9	137	.....	6.6	15.6	1.6	6.9	15.7	1.8
10	140	.....	9.1	18.5	2.2	10.3	19.2	2.1
11	143	.....	14.0	29.6	1.5	12.7	28.7	1.5
		Tobacco and other soils‡						
12	120	Coorg Nulkund Estate Soil I	45.7	62.6	1.4	44.5	60.0	2.6
13	121	Assam Jorhat	9.0	23.8	0.7	10.5	23.4	0.7

* Sent by the agricultural chemist, Bengal.

† Sent by the divisional forest officer, Darjeeling, Bengal.

‡ Sent by Rao Bahadur Biswanath, Imperial agricultural chemist.

TABLE 1—*Concluded*

SOIL NO.	LAB. NO.	LOCALITY	INTERNATIONAL—A METHOD H_2O_2-HCl-NaOH (1 PER CENT SUSPENSION OF 20 GM. SOIL SHAKEN FOR 24 HOURS WITH 8 CC. *N* NaOH)			ALKALINE PERMANGANATE METHOD (1 PER CENT SUSPENSION OF 20 GM. SOIL SHAKEN FOR 6 HOURS WITH 8 CC. *N* NaOH)		
			Clay	Clay + silt	Loss on solution	Clay	Clay + silt	Loss on solution
			per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
		Tobacco and other soils‡—Concluded						
14	122	Madras Guntur Tobacco soil	43.8	56.6	0.9	44.0	57.2	1.6
15	123	Bombay Gujarat, Sursa Tobacco soil	14.9	24.5	0.8	15.6	25.6	1.1
		Black cotton soils§						
16	114	Mahalung (Nira, right bank canal)	56.2	67.9	1.8	57.1	67.9	2.0
17	115	Durgapur (Provara, left bank canal)	52.9	71.9	1.7	54.3	71.4	2.4
18	116	Lohagaon (Provara, left bank canal)	45.7	59.7	1.8	47.6	59.9	3.0
19	117	Nimbut (Nira, left bank canal)	57.1	71.9	1.6	57.2	72.1	2.2
20	118	Velapur (Godavari, right bank canal)	50.3	68.6	1.6	48.9	66.8	2.0
21	119	Sonewadi (Godavari, right bank canal)	49.1	64.4	1.7	49.8	64.2	2.5

§ Sent by Dr. J. K. Basu, soil physicist, Padegaon, Bombay. Soils 16, 19, and 20 contain, respectively, 11.6, 9.6, and 14.3 per cent $CaCO_3$.

with potassium permanganate in the presence of a little sodium hydroxide. Binding materials, such as calcium carbonate, in soil are removed by hydrochloric acid, and the manganese dioxide precipitated in the process of oxidation is removed by sodium bisulfite in the presence of dilute hydrochloric acid.

The soil is filtered and washed with sodium acetate solution, just barely acidified with hydrochloric acid, until free from manganese and sulfate. The excess of sodium acetate in the soil is washed off with water. The soil is then shaken with sodium hydroxide, made up to a definite volume, and subjected to pipette sampling. In the actual experiment, 20-cc. samples were removed from the 10-cm. depth of the suspension at different times depending on temperature as calculated by Puri and Amin (4) on the basis of Stoke's law.

In this paper the applicability of the alkaline permanganate method has been tested on various types of Indian soils and it has been found that the results of analysis obtained by this method are thoroughly reproducible and comparable with those obtained by the International-A method.

EXPERIMENTAL RESULTS AND DISCUSSION

From table 1 it will appear that the results for clay and clay silt obtained by the International-A method and by the alkaline permanganate method agree

TABLE 2

Oven-dry clay and clay + silt in air-dry gypseous soils by different methods*

SOIL NO.	LAB. NO.	LOCALITY AND DESCRIPTION	$CaCO_3$	$CaSO_4$	INTERNATIONAL-A METHOD (WITH ROBINSON'S MODIFICATION FOR SOILS CONTAINING GYPSUM)		ALKALINE PERMANGANATE METHOD		
					Clay	Clay + silt	Clay	Clay + silt	Loss on solution
			per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
22	158	Koil patti, 2–8 ft.	8.6	6.8	49.4	57.8	49.1	57.8	2.0
23	159	Guntur, 6–9 ft.	4.1	1.6	57.5	71.5	58.9	73.2	1.9
24	160	Bellary, 2–6 feet.	13.5	2.0	50.1	63.5	49.7	64.1	1.5

*Soils sent by the Government agricultural chemist, Coimbatore, Madras.

very satisfactorily in all the soils. Percentage loss on solution is almost the same by the two methods.

Soils containing calcium carbonate and gypsum

It will be highly interesting to see whether this particular method may be applied without modification in the case of gypseous soils. Robinson (5) has suggested the following procedures for obviating difficulties of dispersion with gypseous soils:

(*a*) Removing coarse gypsum by passing through a 70-mesh sieve after peroxidizing and before acid treatment.
(*b*) Using a stronger acid.
(*c*) Washing with 10 per cent ammonium acetate.

It is to be noted that although the modification (*a*) suggested by Robinson must be included in the alkaline permanganate method after removal of

organic matter in the case of gypseous soils, the other two modifications, (*b*) and (*c*), are unnecessary, for most of the gypsum present in the soil will be transformed into calcium carbonate as a result of reaction between gypsum and alkaline carbonate produced during oxidation of organic matter by alkaline permanganate. It must be stressed, however, that in the case of gypseous soils 15 cc. of *N* sodium hydroxide, in addition to the alkali required with the permanganate for oxidation of organic matter, should be added gradually for each gram of calcium sulfate contained in the soil.

The results for clay and clay silt shown in table 2 agree very closely for the two methods. The percentage loss on solution is noticeably low. These soils were passed through a 70-mesh sieve after oxidation with alkaline permanganate and before addition of hydrochloric acid to remove coarse gypsum.

TABLE 3

Clay and clay + silt in air-dry soil by different methods

SOIL NO.	LAB. NO.	LOCALITY AND DESCRIPTION	LOSS ON IGNITION	INTERNATIONAL-A METHOD			ALKALINE PERMANGANATE METHOD		
				Clay		Loss on solution	Clay		Loss on solution
				Oven-dried	Ignited		Oven-dried	Ignited	
				per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
25	06	Assam peaty Bheel soil sent by Derby Tea Co.	56.0	22.6	15.2	3.2	25.0	17.6	3.5
26	02	Assam peaty soil sent by Sephinjuri Bheel Tea Co. Ltd.	34.5	35.6	29.1	2.8	37.1	30.9	3.8
				Clay + silt			Clay + silt		
25	..	.....	....	46.1	35.2	...	47.1	35.8	...
26	..	.....	....	62.0	54.5	...	61.1	54.5	...

Soils containing large quantities of organic matter

It was necessary to determine how the soils containing large quantities of organic matter respond to the alkaline permanganate method. For this purpose two soils from Assam having loss on ignition as high as 56 and 36 per cent have been subjected to analysis by both the methods. It has been found that a very large volume of hydrogen peroxide used over about 2 days is required for changing the dark humic color of the soils. Even then the removal of organic matter might not have been so perfect as with the alkaline permanganate, which required about 3 hours to complete oxidation. The results of analysis are given in table 3.

Table 3 shows that although the percentages of clay silt, both oven-dried and ignited, are almost the same by the two methods, the results for clay, both oven-dried and ignited, by the alkaline permanganate method are distinctly

The soil is filtered and washed with sodium acetate solution, just barely acidified with hydrochloric acid, until free from manganese and sulfate. The excess of sodium acetate in the soil is washed off with water. The soil is then shaken with sodium hydroxide, made up to a definite volume, and subjected to pipette sampling. In the actual experiment, 20-cc. samples were removed from the 10-cm. depth of the suspension at different times depending on temperature as calculated by Puri and Amin (4) on the basis of Stoke's law.

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Clay and clay + silt in air-dry soil by different methods

SOIL NO.	LAB. NO.	LOCALITY AND DESCRIPTION	LOSS ON IGNITION	INTERNATIONAL-A METHOD			ALKALINE PERMANGANATE METHOD		
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				per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
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Table 3 shows that although the percentages of clay silt, both oven-dried and ignited, are almost the same by the two methods, the results for clay, both oven-dried and ignited, by the alkaline permanganate method are distinctly

higher than those by the International-A method. Soil 25, i.e., the soil with higher loss on ignition, shows greater difference in clay figures than soil 26. This at once suggests that in these soils dispersion by the alkaline permanganate method has been more complete than by the International-A method. This may be cited as an additional reason for adopting the permanganate method for mechanical analysis of soils. Loss on solution of these soils, as expected, was found to be a little higher than that of other soils.

SUMMARY AND CONCLUSIONS

A method of mechanical analysis using alkaline permanganate for oxidation of organic matter has been found to yield comparable results with the International-A method in the case of various Indian soils, e.g., ordinary arable, forest, gypseous, peat, and lateritic (1) soils. Thus the method appears to be a general method for mechanical analysis of soils. This is particularly suitable for soils rich in organic matter and is recommended for use in tropics where hydrogen peroxide is not very stable.

Alkaline permanganate requires only a short time for oxidation of organic matter.

Soils containing gypsum should be passed through a 70-mesh sieve to remove coarse gypsum after oxidation with alkaline permanganate and before addition of hydrochloric acid.

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DISPERSION OF SOIL FOR MECHANICAL ANALYSIS BY SODIUM CARBONATE OR SODIUM OXALATE TREATMENT

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An examination of existing methods of dispersion, of which many excellent reviews can be found in the literature, reveals the fact that all of them ultimately aim at producing a sodium-saturated soil. In the removal of other exchangeable bases, notably Ca and Mg, whether by HCl treatment (7), NaCl leaching (4), boiling with ammonium carbonate (5), or treatment with sodium carbonate (2) or sodium oxalate (3), the underlying principle is the same, i.e., replacement by Na. Humus if present introduces complications and requires treatment with H_2O_2, but such soils can be easily given special treatment before sodium-saturated soil is produced.

In a previous publication the writer has shown that exchangeable Ca in soils can be completely precipitated as carbonate or oxalate by shaking with a soluble carbonate or oxalate (6). In other words we can convert a Ca-saturated soil into a Na soil by treatment with sodium carbonate or oxalate in quantities equivalent to the exchangeable Ca in it. If we knew the exchangeable Ca and unsaturated acidoid in a soil, it would be a simple matter to add Na_2CO_3 or Na oxalate equivalent to the exchangeable Ca, and NaOH equivalent to the unsaturated acidoid; a sodium-saturated soil would result, and no extraneous chemical would be in excess. The soil in that state will show maximum dispersion.

The extra work involved in the preliminary determination of exchangeable Ca and free acidoid is more than compensated by the fact that the results obtained are valuable in themselves and should prove useful data for any soil under examination. Besides, this determination entails only simple titrations for which the actual working time is much less than that required for most of the preliminary treatments advocated from time to time.

DETAILED DESCRIPTION OF THE PROPOSED METHOD

Ten grams of soil is left with 200 cc. of 0.2 *N* K_2CO_3 in *N* KCl for 1 to 2 hours with occasional shaking. The suspension is then filtered and an aliquot titrated for total alkalinity by adding excess of standard acid, boiling, and back titrating with standard alkali. It can be titrated directly, as well, with methyl red as indicator. The total decrease in acidity is equivalent to the exchangeable Ca+ free acidoid. Another aliquot of the filtrate is titrated for bicarbonates by adding known amounts of standard NaOH and $BaCl_2$ and then

titrating the residual NaOH with standard oxalic acid using thymolphthalein as indicator. Phenolphthalein can be used, but the former gives a sharper end point. The total bicarbonates are equivalent to the free acidoid. It is understood, of course, that the original solution contains no bicarbonate; if it does, this quantity is subtracted from the final value. Total decrease in acidity minus the bicarbonates give exchangeable Ca and sodium carbonate or sodium oxalate equivalent to exchangeable Ca, and NaOH equivalent to free acidoid is added to 10–20 gm. of soil suspended in about 200 cc. of water and shaken over night. Two hours' shaking suffices for most soils, but overnight shaking will ensure maximum dispersion in all types. After being shaken the soil is ready to be made up to the desired volume for the pipette method of mechanical analysis.

ALTERNATE METHOD

An alternate method is based on the potassium oxalate method of estimating exchangeable Ca in soils (6). Ten grams of soil is shaken, by hand, in a stoppered bottle for about half an hour with 100 cc. of the following solution and cooled below 15°C.: *N* with respect to potassium acetate, 0.015 *N* with respect to potassium carbonate, 0.1 *N* with respect to potassium oxalate. The suspension, after being shaken, is filtered and an aliquot of the filtrate titrated with standard permanganate. The total decrease in the concentration of oxalate ion is equivalent to the exchangeable Ca in the given weight of the soil. Sodium carbonate or oxalate equivalent to exchangeable Ca is then added to the soil suspended in about 100 cc. of water. The suspension is then brought to pH 10.5 by adding 0.5 *N* NaOH in 1-cc. lots, shaken vigorously, and tested with thymolphthalein as an external indicator until an intense blue color is produced on a drop of the indicator. It is best to start about a dozen or more soils at a time so that sufficient time can be allowed between incremental additions of alkali. The soil suspension is then shaken overnight and made up to the desired volume for pipette analysis.

It might be pointed out that it is not essential to add exact quantities of oxalate-carbonate or hydroxide equivalent to the exchangeable Ca or acidoid; these quantities can be varied within certain limits without affecting the results. This fact leads to a further simplification of technique when dealing with soils of a similar type from a restricted area. The highest amount of exchangeable Ca and acidoid can be ascertained by examining a number of soils, adding a corresponding amount of carbonate—oxalate and hydroxide, and shaking the suspension overnight.

As regards the relative merits of sodium carbonate or oxalate, no opinion can be expressed; both give similar results, and the choice must be left to the individual worker.

EXPERIMENTAL

The sodium carbonate-oxalate method was compared with the author's NaCl-NaOH method, with the $(NH_4)_2CO_3$ method, and in the case of humus soils

TABLE 1

Clay content of soils by various methods of dispersion

SOIL NUMBER	LOCALITY	CLAY CONTENT			
		NaCl method	$(NH_4)_2CO_3$ method	Na_2CO_3 method	$Na_2C_2O_4$ method
		per cent	*per cent*	*per cent*	*per cent*
	Ordinary agricultural soils				
1	Pusa (Bihar)	11.3	13.7	11.9	9.8
4	Ranala I (Punjab)	15.2	18.1	14.3	13.2
5	Ranala II (Punjab)	12.3	14.8	12.4	11.7
8	Coimbator I (Madras)	25.2	25.7	24.9	26.1
10	Coimbator II (Madras)	35.6	37.0	36.7	37.7
11	Coimbator III (Madras)	32.8	31.0	33.2	33.3
17	Kalyanpur (U. P.)	11.9	17.5	10.7	10.0
19	Mandalay (Burma)	42.4	44.2	42.5	41.3
21	Kaing (Burma)	13.5	16.4	11.2	12.1
23	Myetha (Burma)	11.3	11.8	10.2	9.8
26	Hebbal (Mysore)	22.6	20.5	17.2	21.3
28	Nagpur (C. P.)	44.6	44.6	47.7	40.9
31	S. Travancore	22.8	28.1	22.3	22.6
34	Gurdaspur (Punjab)	11.3	15.5	10.1	11.6
35	Gurgaon (Punjab)	18.3	18.3	14.7	16.6
36	Hansi (Punjab)	11.7	14.4	10.4	10.3
43	Churland (Bihar)	19.7	24.7	20.3	20.8
44	Highland (Bihar)	8.4	13.2	8.3	9.7
48	Montgomery I (Punjab)	19.8	24.8	18.6	20.2
50	Tarnab I (N. W. F. P.)	17.7	19.6	17.2	17.8
51	Tarnab II (N. W. F. P.)	12.9	13.9	13.3	13.0
52	Sabour (Bihar)	11.3	10.0	9.2	8.4
54	Montgomery II (Punjab)	3.2	6.2	4.2	4.2
55	Sakrand I (Sindh)	11.0	14.9	12.1	12.2
56	Sakrand II (Sindh)	13.1	17.5	18.2	15.8
59	Raghopur (U. P.)	10.9	12.2	9.3	9.0
	Black cotton soils				
2	Akola (Bombay)	59.3	62.8	59.0	60.3
3	Dharwar (Bombay)	62.2	63.8	63.9	65.0
13	Nagpur (C. P.)	58.9	60.4	60.5	57.7
27	Babhur (Mysore)	53.2	59.1	54.1	57.9
29	Jabbalpur (C. P.)	63.0	57.4	64.0	64.7
30	Hoshangabad (C. P.)	54.1	55.1	54.6	56.6
41	Poona (Bombay)	53.4	61.6	57.0	57.7
42	Khandesh (Bombay)	53.4	58.9	58.8	61.2
46	Baroda (Bombay)	56.6	59.0	58.0	60.2

TABLE 1—*Concluded*

SOIL NUMBER	LOCALITY	CLAY CONTENT			
		NaCl method	$(NH_4)_2CO_3$ method	Na_2CO_3 method	$Na_2C_2O_4$ method
		per cent	*per cent*	*per cent*	*per cent*
	Lateritic and ferruginous soils				
6	Dacca (Bengal)	28.4	31.6	30.4	29.3
9	Malabar (Madras)	21.6	22.8	22.6	24.3
12	Tocklai (Assam)	3.8	14.8	9.8	9.1
14	Estate Soil (Madras)	11.1	31.5	34.7	35.6
15	Shillong (Assam)	19.4	27.6	25.6	29.5
18	Mandalay (Burma)	19.9	25.2	19.8	20.1
20	Lower Burma	6.5	15.1	10.6	8.2
22	Pyrinana Soil (Burma)	15.2	17.8	14.0	13.3
25	Bhur Soil (U. P.)	4.0	5.8	4.2	3.8
37	Rangpur (Bengal)	4.2	15.3	6.6	7.9
40	Umareth (Bombay)	13.1	17.0	12.3	13.9
45	Bihar	10.7	14.0	10.5	8.6
49	Madhupur (Bihar)	27.3	32.6	26.3	27.1

with the International method. Altogether, 56 soils, comprising practically all the types found in India, were examined. For convenience of reference, they are grouped as follows: ordinary agricultural soils, black cotton soils, lateritic and ferruginous soils, humus soils.

The results are given in tables 1 and 2.

DISCUSSION OF RESULTS

If the highest clay percentage obtained by any method be the criterion, then the $(NH_4)CO_3$ method appears to be the most efficient. It was found, however, that for some soils even H_2O_2 treatment failed to give as much dispersion as that obtained with $(NH_4)_2CO_3$. This raised the doubt that in certain soils $(NH_4)_2CO_3$ might bring into suspension material other than clay, and the high alkalinity of the medium would lend support to this view.

The sodium carbonate-oxalate method produced maximum disperson in all soils except the humus soils. Even those soils that responded poorly to the NaCl-NaOH method gave very good results with this method.

The sodium carbonate-oxalate method is of particular interest, for apart from its extreme simplicity it has a theoretical background which places the whole question of clay dispersion on a sounder footing. It affords us for the first time the true explanation of the empirically discovered superiority of sodium carbonate and sodium oxalate for dispersing soils and the cause of their failure when not used in the right quantities. The work of Chakraborty and Sen (1), who showed that laterite soils require only shaking with NaOH to give maximum dispersion, is also brought into line with the logical deductions of the principle involved in the present method. Laterite soils are highly unsaturated

soils which contain very little exchangeable Ca. Such soils, therefore, require only neutralization of the acidoid with NaOH to attain maximum dispersion.

Humus soils are the only type which fails to respond to the sodium carbonate-oxalate method (table 2). The cause of this failure seems to lie in the mechanical difficulty of breaking up the clay-humus aggregate. Clay in highly humus soils is more or less enveloped in a humus layer which must be broken down mechanically to enable the clay particles to go into suspension. The action of H_2O_2 in the oxidation of humus, as far as the dispersion of clay is concerned, is still not well understood. No doubt some oxidation takes place, but the loss on ignition of the oven-dry clay determined after the H_2O_2 treatment indicates that the portion actually destroyed is immaterial.

The only modification in the sodium carbonate-oxalate method to suit humus soils is as follows: After the addition of the right quantities of sodium carbonate or oxalate and hydroxide, the soil suspended in 100–200 cc. of water is boiled

TABLE 2

Clay content of humus soils

SOIL NUMBER	LOSS ON IGNITION	CLAY CONTENT							
		Na_2CO_3 method		$Na_2C_2O_4$ method		H_2O_2 method		$(NH_4)_2CO_3$ method	
		Oven dry	Ignited	Oven dry	Ignited	Oven dry	Ignited	Oven dry	Ignited
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
75	50.1	24.4	9.2	18.2	5.8	37.2	15.0	36.7	15.5
76	35.7	14.2	5.7	17.3	7.1	29.7	18.3	29.4	15.5
78	13.1	15.1	9.6	17.5	10.4	25.7	19.9	30.1	16.0
79	12.3	14.2	8.7	16.1	9.8	26.0	20.0	27.5	19.6
81	35.9	18.0	6.8	20.2	7.5	31.2	15.3	28.6	20.2
84	32.2	11.5	5.3	13.6	5.8	28.5	15.7	32.0	17.8
86	29.9	12.1	5.2	14.0	6.2	23.8	16.4	34.2	15.3
87	28.7	12.6	5.9	13.8	6.2	27.3	13.9	27.9	19.7

for 1 to 2 hours, with small quantities of H_2O_2 or $(NH_4)_2CO_3$ added at intervals to keep up a brisk boiling. The disruption of the clay humus complex is effected by bubbles of oxygen in the one case and by CO_2 in the other. Frothing can be prevented by the addition of a little mineral oil.

As will appear from the loss on ignition of humus soils given in table 2, soils were specially selected with very high humus content to put the proposed method to an extremely rigid test. Ordinarily, soils with such a high humus content, when shaken with KCl-K_2CO_3 for the preliminary estimation of exchangeable Ca and free acidoid, yield a colored filtrate. However, with a certain amount of dilution and back titration technique and the use of brom thymol blue as indicator there is generally no difficulty in locating the end points with reasonable accuracy. As has been pointed out, it is not necessary to add exact amounts of reagents for final dispersion.

Clay in humus soils is generally recorded on the ignited weight basis. This practice is open to objection as the loss on ignition is not a fixed constant but

must vary with the manner in which ignition is carried out. This will produce lack of uniformity of results in the hands of different workers. Humus itself would leave on ignition a mineral residue that could not be classed as clay by any stretch of imagination. The practice of taking the ignited weight evidently started with the object of rigidly excluding everything that was not clay; but it is bound to lead to a distorted vision of the true state of affairs. For all practical purposes humus is as good a clay as clay can be. It shows base exchange, moisture absorption, and other related properties like clay and therefore must be classed as clay. Besides, its manner of dispersion is not fundamentally different from that of clay, and the results obtained are just as reproducible. From the practical point of view, also, humus plays as important a rôle as clay, and there is no reason why it should not be reckoned as such. In table 2 are recorded both the ignited and the oven-dry weights. It will be seen that results on the oven-dry basis with the H_2O_2 and $(NH_4)_2CO_3$ treatment show a good agreement, indicating that in both cases we are measuring a fundamental constituent of the soil and not something that is produced as the result of a particular treatment.

It is obvious that soils containing excessive amounts of soluble salts or gypsum cannot be dispersed by any single treatment, for the salts will appear as clay even if the soil does not become flocculated. Such soils must be first leached with water to rid them of soluble salts and then shaken with $BaCO_3$ to make the calcium sulfate ineffective (6).

SUMMARY

The proposed method consists in the estimation of exchangeable Ca and free acidoid, sodium carbonate or oxalate equivalent to the former and sodium hydroxide equivalent to the latter being subsequently added and the soil suspension shaken overnight.

To attain maximum dispersion, soils rich in organic matter require boiling with H_2O_2 or ammonium carbonate in addition to the foregoing treatment.

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BEHAVIOR OF POLYVALENT CATIONS IN BASE EXCHANGE[1]

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The theoretical and practical significance of base exchange in soil formation and in plant nutrition has been fully discussed in previous papers (2, 4). The present study aims to ascertain further the rôle played by various cations in the exchange process. Emphasis is laid on carefully standardized and controlled experimental conditions in order to permit quantitative comparisons of the replacing power of the electrolytes investigated.

EXPERIMENTAL TECHNIQUE

In general, the technical procedure employed was the same as that reported in earlier publications (1). Clays extracted from the subsoil of the Putnam silt loam were electrodialyzed, and the H-clays thus formed converted into basic clays by addition of hydroxides, except in the case of La- and Th-clays which were obtained by leaching of NH_4-clay with $La(NO_3)_3$ and $ThCl_4$. In all experiments 7.5 gm. of colloidal Putnam clay (weight expressed as H-clay) containing 4.50 m.e. exchangeable cations was put into a 500-cc. flask, a known amount of electrolyte added, and the container filled to the mark with doubly distilled water. After a reaction time of one week, during which the flasks were kept in a constant temperature room (28 ± 1°C.), the extent of the exchange was determined from analyses of the supernatant liquid.

TABULATION OF DATA

The results obtained are reported in tables 1–5. To economize in space, only the initial electrolyte concentrations and the corresponding exchange values are given. Any desired equilibrium value can be easily computed from these data. The amount of electrolyte added is expressed in terms of symmetry concentrations (S), viz., multiples of the milliequivalents of exchangeable ions in the colloidal system. For the clay concentrations used, 1S corresponds to 4.50 m.e. of electrolyte per 500 cc. volume. The exchange is listed as percentage of adsorbed ions replaced (4.50 m.e. = 100 per cent).

[1] Contribution from the department of soils, Missouri Agricultural Experiment Station, Journal Series No. 475.

[2] The authors are indebted to the National Research Council for a grant-in-aid in 1933. The work was completed in 1934, but publication had to be delayed.

TABLE 1

Ionic exchange with NH_4-clay

(Released NH_4 ions determined)

NATURE OF ELECTROLYTE ADDED	IONIC EXCHANGE VALUES FOR THE FOLLOWING SYMMETRY CONCENTRATIONS			
	½	1	2	4
LiCl	20.56	29.89	44.44	54.67
NaCl	20.56	(35.33)	45.11	54.89
KCl	32.78	51.33	66.78	75.22
RbCl	41.11	62.56	80.22	90.00
CsCl	51.33	68.78	85.33	90.00
HCl	50.44	84.89	90.89	90.89
$MgCl_2$	48.67	65.44	71.29	78.37
$CaCl_2$	45.44	63.56	75.33	80.00
$SrCl_2$	52.22	69.44	77.00	82.67
$BaCl_2$	52.67	71.67	77.00	83.11
Luteo chloride (3 valent) (cobalt determined)	48.8	96.1	102.4	103.8
$ThCl_4$	46.00	80.89	92.22	92.44
Methylene blue	.....	83.33	.....	.....

TABLE 2

Ionic exchange with Ca-clay

(Released Ca ions determined)

NATURE OF ELECTROLYTE ADDED	IONIC EXCHANGE VALUES FOR THE FOLLOWING SYMMETRY CONCENTRATIONS			
	½	1	2	4
LiCl	9.49	13.08	19.52	27.45
NaCl	9.08	12.74	19.72	30.16
KCl	18.98	28.80	42.29	59.37
NH_4Cl	18.91	29.35	43.99	62.42
RbCl	28.46	43.85	63.03	80.99
CsCl	30.94	50.83	70.07	89.90
HCl	47.57	77.80	87.80	89.19
$MgCl_2$	32.11	47.53	63.32	76.67
$BaCl_2$	35.13	52.96	67.00	80.78
$ThCl_4$	42.90	80.24	95.56	99.35
Methylene blue	.....	77.94	.....	.....

TABLE 3

Ionic exchange with K-clay

(Released K ions determined)

NATURE OF ELECTROLYTE ADDED	IONIC EXCHANGE VALUES FOR THE FOLLOWING SYMMETRY CONCENTRATIONS			
	½	1	2	4
HCl	52.36	84.44	86.53	95.43
$CaCl_2$	43.70	60.30	76.42	72.17
$La(NO_3)_3$	49.72	83.48	87.49	86.85
$ThCl_4$	47.85	82.88	90.57	90.89

NATURE OF EQUILIBRIUM

The data in tables 1–5 reveal that the base exchange equilibrium is not always a true one. Different exchange values are obtained for the left hand

TABLE 4

Ionic exchange with H-clay

NATURE OF ELECTROLYTE ADDED	IONIC EXCHANGE VALUES FOR THE FOLLOWING SYMMETRY CONCENTRATIONS			
	½	1	2	4
LiCl	4.5	6.6	9.0	13.0
NaCl	3.5	6.2	9.8	13.5
KCl	8.6	14.5	26.0	34.2
RbCl	19.01	28.20	41.22	62.16
CsCl	25.20	39.73	60.24	82.88
	EXCHANGE DETERMINED BY ANALYSES OF THE DI-VALENT CATION BEFORE AND AFTER EXCHANGE			
$MgCl_2$	10.67	15.78	22.44	.....
$CaCl_2$	17.33	26.89	44.00	.....
$SrCl_2$	30.22	.....	.....	.....
	24.44	34.55	54.67	.....
$BaCl_2$	16.00	23.78	34.44	.....

TABLE 5

Ionic exchange with poly-clays and chlorides

(Outgoing ion determined)

NATURE OF CLAY	NATURE OF ELECTROLYTE ADDED	IONIC EXCHANGE VALUES FOR THE FOLLOWING SYMMETRY CONCENTRATIONS			
		½	1	2	4
Mg-clay	KCl	20.95	31.32	45.28	63.04
Mg-clay	HCl	50.27	79.79	88.77	94.35
Mg-clay	$BaCl_2$	28.73	50.27	71.01	83.58
Sr-clay	KCl	16.40	25.76	39.38	54.22
Sr-clay	HCl	43.31	68.93	78.89	82.15
Ba-clay	KCl	17.61	26.75	39.89	57.32
Ba-clay	HCl	45.99	71.03	83.60	88.36
La-clay	KCl	9.62	13.96	21.34	33.74
Th-clay	KCl	1.85	1.85	3.11	5.56

and the right hand approach of the final state. When, for example, the system

$$\boxed{\text{clay}}\ Ca + 2KCl \rightleftharpoons \boxed{\text{clay}}^{K}_{K} + CaCl_2$$

is considered, it is found that at symmetry concentrations 28.8 per cent Ca from Ca-clay is replaced by addition of KCl, whereas 60.2 percent K is released from

K-clay + $CaCl_2$. The sum of the two values is only 89.0 per cent instead of 100 per cent. The discrepancy is particularly noticeable in exchange reactions involving both monovalent and polyvalent cations (e.g., Th-systems). These data confirm the observations of Vanselow (5), who is of the opinion that the phenomenon, which he calls "hysteresis," is associated with the crystal structure of the colloidal particle.

DEFINITION OF ADSORPTION

The term "adsorption" as used in this paper designates a change in ion concentration in the surface without any implication regarding the nature of the forces active in the reaction. If we state that a particular ion has been "adsorbed" we merely indicate that the concentration of that ion in the solid phase has been increased. The adsorbed ions may or may not be exchangeable. If they are exchangeable we assume that the exchange reaction is stoichiometric.

BEHAVIOR OF MONOVALENT CATIONS

The adsorption of monovalent cations by mono- and poly-clays yields typical lyotropic series (fig. 1) which can be described as follows:

$$Li \lessgtr Na < K < NH_4 < Rb < Cs < H$$

The peculiar crossing of the Li and Na curves confirms previous observations (2). An important result of the present study is the fact that the lyotropic series of the monovalent ions appears to be a characteristic property of a given colloidal clay system. The relative sequence of the ions within the series remains the same whether the system is an NH_4-clay, a H-clay, or a Ca-clay. The release of surface ions produces a series which is exactly the reverse of the adsorption order. Again, the series is independent of the nature of the cation which brings about the release.

These results lead one to believe that monovalent cations adsorbed on clay surfaces possess certain characteristic properties (e.g., ion hydration, oscillation space, etc.), which are not greatly influenced by the neighboring exchangeable cations.

BEHAVIOR OF POLYVALENT IONS

The polyvalent ions studied comprise di-, tri-, and tetravalent cations, all of rare gas type. Although we analyzed a considerable number of exchange reactions, the data at hand are not numerous enough to permit enunciation of generalized principles because the ions seem to act in an irregular manner.

Figure 2 shows exchange isotherms for NH_4-clay systems (compare table 1) whereas figure 6 depicts the results with K-clays (compare table 3). From these data the lyotropic series for polyvalent ions can be ascertained. It is as follows:

$$Mg \lessgtr Ca < Li < Ba < La < Th$$

The position of the two lowest members of the series, Mg and Ca, becomes reversed with increasing electrolyte concentration, a feature also observed for the first two ions in the monovalent series (Li, Na). Generally speaking, the curves for the divalent ions assemble themselves into a relatively closely packed bundle of lines, and in this respect the Putnam clay differs significantly from the permutite systems previously investigated (fig. 3). Unlike the monovalent ions the divalent ones do not produce consistent adsorption series, as seen from the following tabulation:

NH_4-clay gives the order Mg $\lessgtr$ Ca < Sr < Ba,
H-clay gives the order Mg < Ba < Ca < Sr,
Ca-clay gives the order Mg < Ca < Ba.

In the case of H-clay, Ba has shifted to a lower position, and the Mg- and Ca-curves do not overlap.

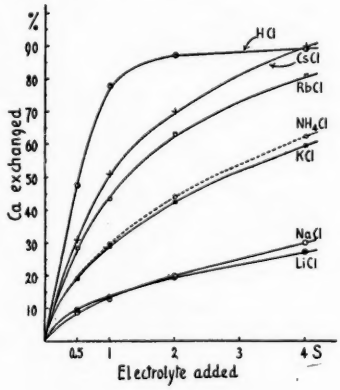

FIG. 1

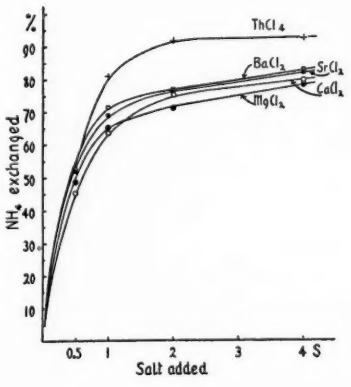

FIG. 2

FIG. 1. EXCHANGE ADSORPTION OF MONOVALENT CATIONS BY Ca-CLAY
FIG. 2. EXCHANGE ADSORPTION OF DIVALENT AND TETRAVALENT CATIONS BY NH_4-CLAY

In the process of release of adsorbed divalent cations the irregularities observed during intake become amplified. A few typical examples may serve as illustrations. If Mg-, Ca-, Sr-, and Ba-clays are treated with KCl or with HCl, the divalent ions come out in the order

$$Sr < Ba < Ca < Mg,$$

which differs from the negative adsorption series in that Sr and Ba are not reversed. Exchange of Mg-clay and Ca-clay with $BaCl_2$ produces the relation Mg $\lessgtr$ Ca, according to which the Mg-curve and the Ca-curve cross each other (fig. 4). At low electrolyte concentration Mg appears to be held more tightly than Ca, whereas at higher salt concentration the reverse is true. At present it appears difficult to furnish an explanation of these irregularities.

INFLUENCE OF IONIC SIZE

There are two comparable sets of results which permit one to evaluate the rôle of ionic diameters in base exchange. The two systems are

NH_4-clay + monovalent cations (Li, Na, K, Rb, Cs), and
NH_4-clay + divalent cations (Mg, Ca, Sr, Ba).

In figure 5 the symmetry values have been plotted against the *ionic radii* (crystal lattice radii of Goldschmidt). For both systems an S-shaped curve is the characteristic feature of the base exchange-ionic size relationships. A still more pronounced wave nature is observed for the curves of Ca-clay and H-clay, the data of which are contained in tables 2 and 4.

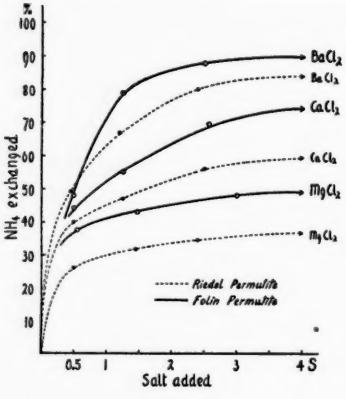

FIG. 3

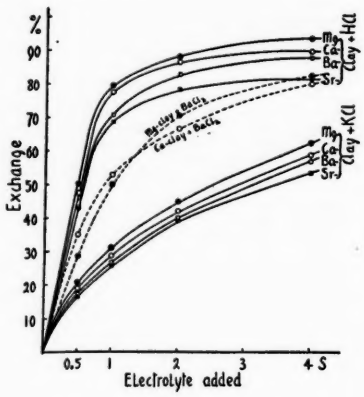

FIG. 4

FIG. 3. ADSORPTION OF DIVALENT IONS BY TWO NH_4-PERMUTITES
Note the wide spread of the curves as compared with NH_4-clay in figure 2

FIG. 4. RELEASE OF DIVALENT IONS (MG-CLAY, CA-CLAY, ETC.) BY MONO- AND DIVALENT CATIONS

With Wiegner, we believe that the hydration of ions offers at present the best explanation of the lyotropic series. Wiegner's original concept, however, needs slight modification in that the hydration of ions assumes different magnitudes in different silicate systems and thus cannot be directly related to hydration values of ions in dilute solutions. In Putnam clays the small ions (Li, Mg) act as if they were partially dehydrated.

Recently, certain Dutch investigators [Verwey (6), Bär (1)] have suggested that the lyotropic series can be explained by polarization of ions, thus eliminating the hydration concept, which, as is admitted, is not satisfactory in all respects. Calculations show, however, that the attraction energy due to ion polarization is only a fraction of the straight Coulombic attraction, and thus unable to reverse the lattice radii series. From the publications at hand it is not quite clear how the aforementioned investigators visualize the

origin of the observed lyotropic series on the basis of polarizability of the exchangeable ions.

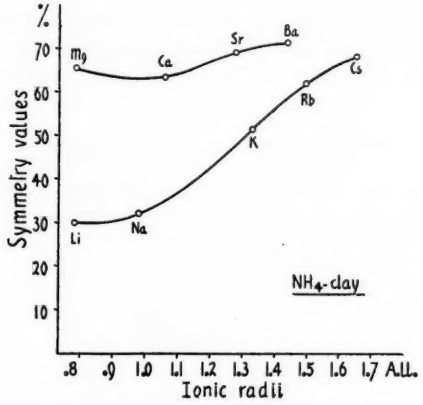

FIG. 5. EXCHANGE INTENSITIES PLOTTED AS A FUNCTION OF THE RADII OF THE ADSORBED IONS

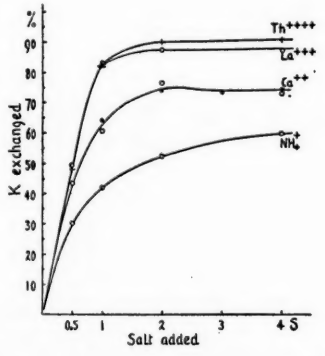

FIG. 6

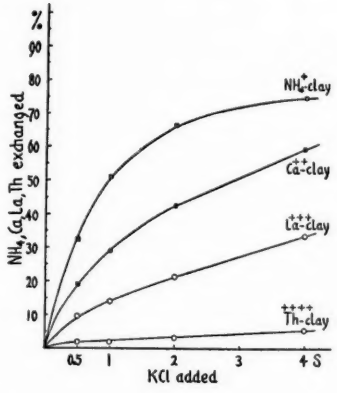

FIG. 7

FIG. 6. EFFECT OF ELECTRIC CHARGE OF IONS ON THE ADSORPTION INTENSITY
K-clay treated with chlorides

FIG. 7. RELEASE OF ADSORBED MONO- AND POLYVALENT CATIONS BY KCl

INFLUENCE OF THE ELECTRIC CHARGE OF IONS OF SIMILAR SIZE

For ions of similar size the adsorption intensities can be correlated with the electric charge. The present study permits the comparison of the following ions, the radii of which are given in parenthesis (Angstrom units):

K^+ (1.33), NH_4^+ (1.43), Ca^{++} (1.02), La^{+++} (1.22), Th^{++++} (1.10)

Potassium and ammonium ions are very similar in size and behave practically alike in the exchange process (*see* fig. 1). Table 3 contains the experimental data for the adsorption of Ca, La, and Th by K-clay, whereas the values for the system K-clay + NH_4Cl are contained in a previous publication (1). Unfortunately these earlier data are not strictly comparable with the present ones. The curves are shown in figure 6; it is evident that the order of ions in adsorption is as follows:

$$NH_4^+ < Ca^{++} < La^{+++} < Th^{++++}$$

The higher the charge of an ion, the better it is adsorbed. The effect of valency on the release can be studied from the following systems:

NH_4-clay + KCl (table 1)
Ca-clay + KCl (table 2)
La-clay + KCl (table 5)
Th-clay + KCl (table 5)

The exchange curves are represented in figure 7, according to which the order of release takes the following form

$$Th^{++++} < La^{+++} < Ca^{++} < NH_4^+$$

It is the reverse of the adsorption series. Monovalent NH_4^+ comes out most easily; Th^{++++}, with four electric charges, is released with great difficulty. All clays are negatively charged (4).

SUMMARY

A study has been made to ascertain the rôle of mono- and polyvalent cations in base exchange reactions with Putnam clay. Although the behavior of the ions is irregular, it appears that the electric charges and the sizes of the ions are two of the major factors which determine the position of an ion in the adsorption and release series.

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THE EFFECT OF PHOSPHATES ON THE CATION EXCHANGE CAPACITY OF CERTAIN SOILS[1]

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The literature on base exchange studies on soils has been voluminous in recent years. The earlier work by men like Kelley (8), Chapman (6), Schollenberger (25), Pierre (18), and Puri (20) was largely concerned with methods of studying replaceable bases. Then followed work on the nature of base exchange material (9, 10, 11), the relation of exchangeable cations to the physical properties of soil (2), and the intricate relation between cation and anion exchange with aluminum, iron, and silicate complexes (3, 12, 15).

In all these studies the phosphates play a very important rôle, and the literature on the subject of the mechanism of phosphate adsorption or retention is growing tremendously. The work of Scarseth (23, 24), Ravikovitch (21), Roszman (22), and Mattson (15) may be cited in this connection.

Recently the authors of this paper have been carrying on base exchange studies on soils that have received various nitrogenous fertilizers, especialy ammonium compounds. In addition to receiving different nitrogen fertilizers, these soils have been receiving three different applications of superphosphate. This fact suggested the possibility of studying the relation between the cation exchange capacity of a soil and the amount of phosphates applied. Sassafras silt loam soil from one of the cylinder experiments at the New Jersey Station, where different nitrogenous materials have been applied annually since 1922, was used in this study. Originally the soil was strongly acid, having a pH of 5.3. This acid condition was corrected by the use of ground limestone to bring the reaction to about 6.6–7.0. At intervals during the 14-year period of this experiment lime has been applied when the pH value of the soil dropped to about pH 6.0 or a little lower. Unfortunately, about 2 years ago the pH value of the soil on section C had dropped to about 5.0. At that time ground limestone was applied to bring the pH to 6.6–7.0. No lime was applied to sections D and E and as a consequence these are becoming more acid, and at the present time are about 0.2 to 0.3 of a pH unit below 6, whereas the pH of the soil in section C is close to pH 6.5. These fluctuations in pH should be taken into consideration when the exchangeable hydrogen and base exchange data are studied.

[1] Journal Series paper of the N. J. Agricultural Experiment Station, department of soil chemistry and bacteriology.

The experiment was planned to furnish nitrogen, in equivalent amounts, from nitrate of soda, sulfate of ammonia, dried blood, and also from a mixture of the three (one-third of the nitrogen from each). The nitrogen materials were used in amounts equivalent to 320 pounds of nitrate of soda to the acre. Also, provision was made for supplying phosphorus in the form of 16 per cent superphosphate in three different amounts; namely, at the rate of 320, 640, and 960 pounds to the acre (10, 20, and 30 gm. per cylinder). Potash was used as C.P. potassium chloride to give 50 pounds of K_2O to the acre.

The arrangement of the cylinders in pairs with the fertilizer treatment is as follows:

SOURCE OF NITROGEN	SECTION	SINGLE PORTION P_2O_5	DOUBLE PORTION P_2O_5	TRIPLE PORTION P_2O_5
No nitrogen (check)	A	○ ○	○ ○	○ ○
Nitrate of soda	B	○ ○	○ ○	○ ○
Sulfate of ammonia	C	○ ○	○ ○	○ ○
Dried blood	D	○ ○	○ ○	○ ○
⅓ nitrogen from each	E	○ ○	○ ○	○ ○

PLAN OF RESEARCH

Soil samples were collected from the cylinders the latter part of March, 1936, and composites made of the duplicate cylinders. First, pH determinations were made on the moist samples by the electrometric method using a Leeds and Northrup glass electrode. The soils were then air-dried and put through a 2-mm. sieve. The total base exchange capacity and exchangeable hydrogen on these soils were then determined by the barium acetate extraction method. At the same time duplicate samples were extracted with normal neutral ammonium acetate solution for the determination of the individual cations.

BARIUM ACETATE METHOD FOR DETERMINATION OF EXCHANGEABLE HYDROGEN AND TOTAL CATION EXCHANGE CAPACITY

A 10-gm. sample of soil was leached on a 12.5-cm. Whatman filter paper with successive portions of normal barium acetate solution (adjusted to the neutral point) to 500 cc. A 50-cc. aliquot of the extract was then titrated electrometrically using 0.05 *N* ammonium hydroxide. From these data the

exchangeable hydrogen was calculated. A few cubic centimeters of barium chloride solution was then added to the extracted soil, and the excess barium washed out with water, as indicated by the absence of chlorides. The soil was next extracted with 0.05 *N* hydrochloric acid until free from barium (500 cc.). The barium was determined in a 100-cc. aliquot by the addition of 2 per cent sulfuric acid. From the weight of barium sulfate obtained, the total cation exchange capacity was calculated.

AMMONIUM ACETATE EXTRACTION FOR THE DETERMINATION OF CATIONS

A 25-gm. sample of soil was weighed out into a wide-mouth Erlenmeyer flask and 150 cc. of normal ammonium acetate solution (adjusted to the neutral point) added. The flasks were stoppered and shaken occasionally during the day and allowed to stand overnight. Then they were decanted on 15-cm. Whatman filter paper, and filtered into 500-cc. volumetric flasks. After being washed and decanted several times with the ammonium acetate solution, the total soil was transferred to the filter paper. The extraction was continued up to a volume of 500 cc. The extract was evaporated to dryness with 100 cc. of nitric acid, and the ammonium salts were removed by careful ignition. After the residue had been taken up with dilute hydrochloric acid, the silica was removed by dehydration in the usual manner. If iron and aluminum were present they were removed in the usual way with ammonium hydroxide. Manganese, if present, may be removed or determined by the bromine method. The solution was then made up to a definite volume, and aliquot portions were used for the determination of calcium, magnesium, potassium, and sodium.

The calcium was determined by the oxalate precipitation with subsequent titration with 0.05 *N* potassium permanganate.

The magnesium was determined gravimetrically as magnesium pyrophosphate.

The potassium was determined by the method of Schueler and Thomas (26). This is a volumetric method consisting of titration of the precipitated potassium cobaltinitrite with standard potassium permanganate.

The sodium was determined gravimetrically by the uranyl-zinc acetate method of Barber and Kolthoff (1).

In addition to the aforementioned determinations, organic matter was determined on these soils by the wet oxidation method of Tiurin (27).

Most of the analytical data on these soils are recorded in table 1. The averages show the effect of phosphates on the ultimate pH of a soil and on the base exchange capacity. The ultimate pH values were determined only on a composite sample of the soils for each application of phosphorus. In determining the ultimate pH, 50 gm. of the composite soil sample was electrodialyzed for about 72 hours in a Mattson cell (13). When no more bases were present in the cathodic liquid the electrodialysis was considered complete (the cathodic liquid would then be acid to phenolphthalein). The soil was removed from

the cell, dried at a temperature between 50–60°C., and then made up as a 1:2 distilled water suspension. The pH of the suspension was determined by the glass electrode method.

DISCUSSION OF RESULTS IN TABLE 1

It will be noted in table 1 that the pH values on sections A, B, and C were between 6 and 7, whereas on sections D and E, they were slightly below pH 6.0

TABLE 1

Base exchange and pH data on soils from cylinder M

(Base exchange results expressed in m.e. per 100 gm. of soil)

CYLINDER NUMBER	PO_4 APPLICATION	pH		EXCHANGE H	TOTAL CATION EXCHANGE CAPACITY		Ca	Mg	K	Na	PER CENT CARBON
		Field	Ultimate		Ba-acetate method	NH_4-acetate method					
1A, 2A	Single portion superphosphate	6.25		1.54	7.24	6.14	3.90	0.45	0.13	0.12	1.55
1B, 2B		6.48		1.32	6.81	6.11	4.26	0.30	0.09	0.14	1.63
1C, 2C		6.52		1.10	7.02	5.46	3.68	0.55	0.06	0.07	1.74
1D, 2D		5.64		2.88	6.98	6.17	2.93	0.19	0.10	0.07	1.56
1E, 2E		5.70		1.98	6.68	5.17	2.73	0.29	0.10	0.07	1.53
Average		6.11	4.63	1.76	6.94	5.81	3.50	0.35	0.10	0.09	1.60
3A, 4A	Double portion superphosphate	6.27		1.98	7.02	6.81	4.30	0.36	0.11	.06	1.53
3B, 4B		6.58		1.98	6.98	5.52	3.09	0.32	....	0.13	1.56
3C, 4C		6.48		2.42	7.36	7.25	4.18	0.53	0.08	0.04	1.63
3D, 4D		5.87		3.52	7.15	6.72	2.97	0.13	0.10	....	1.61
3E, 4E		5.84		3.30	7.49	6.43	2.73	0.26	0.08	0.06	1.52
Average		6.13	4.44	2.64	7.20	6.54	3.45	0.32	0.09	0.07	1.57
5A, 6A	Triple portion superphosphate	6.32		3.08	8.39	6.65	2.97	0.47	0.08	0.05	1.49
5B, 6B		6.63		3.52	8.31	7.21	3.01	0.46	0.08	0.14	1.46
5C, 6C		6.48		3.52	8.01	7.31	3.38	0.26	0.10	0.05	1.65
5D, 6D		5.88		4.84	8.39	7.99	2.78	0.16	0.13	0.09	1.67
5E, 6E		6.01		4.84	7.88	8.06	2.93	0.16	0.08	0.05	1.54
Average		6.20	4.15	3.96	8.19	7.45	3.01	0.30	0.09	0.07	1.56

On section C, where ammonium sulfate was used the pH was about 6.5, due to the extra liming in 1934. Section B, or the nitrate of soda treated cylinders, showed the highest pH values, and sections D and E, the lowest. The effect of doubling and tripling the amount of phosphorus seemed to have little effect on the pH values. If anything, the effect has been to raise the pH values slightly, 0.1 or 0.2 of a pH unit. The average pH value for the single phosphate application was 6.11; for the double, 6.13; and for the triple, 6.20. These averages

were obtained by converting the individual pH values to their corresponding H-ion concentrations, and recalculating the average back to pH terms.

The exchangeable hydrogen was, however, markedly affected by the phosphate treatment. Thus, from the single portion of phosphorus added between 1 and 2 m.e. of exchangeable hydrogen was found per 100 gm. of soil; from the double portion, between 2 and 3.5 m.e., and from the triple portion, between 3 and 4.8 m.e. Each of the cylinders receiving a different form of nitrogen showed a progressive increase in exchange hydrogen as the phosphate application increased. Furthermore, the cylinders receiving the dried blood (section D) showed the greatest exchange hydrogen, probably partly because the pH values of these cylinders were the lowest.

The total cation exchange capacity by the barium acetate method showed a distinct increase when the phosphate applications were doubled or tripled. The average for the single portion was 6.94 m.e. per 100 gm. soil; for the double portion, 7.20 m.e.; and for the triple, 8.19 m.e. This fact is still more strongly emphasized in the results of the total cation exchange by the ammonium acetate method. Here the total m.e. of cations extracted were not so great as with the barium acetate method, but the differences in total exchange capacity for the three phosphate applications were more marked. The average for the single phosphate application was 5.81 m.e. per 100 gm. soil; for the double portion, 6.54; and for the triple portion, 7.45. These findings corroborate those of other investigators. Thus, for example, Merkle (17) found from base exchange studies of the Pennsylvania Jordon field plots that "the continued use of a mixture of superphosphate and muriate of potash when compared with the check plots has resulted in an increase in total exchange capacity. The fertilizer combination has decreased the replaceable calcium and increased the hydrogen content. Magnesium is unaffected but potassium is decidedly increased." Merkle states further: "Superphosphate alone caused neither increase nor decrease in calcium but did increase exchange hydrogen. This fertilizer has resulted in a diminution of magnesium and potassium which is believed to be due to larger crop removals than the check plots. Superphosphate increases soil acidity."

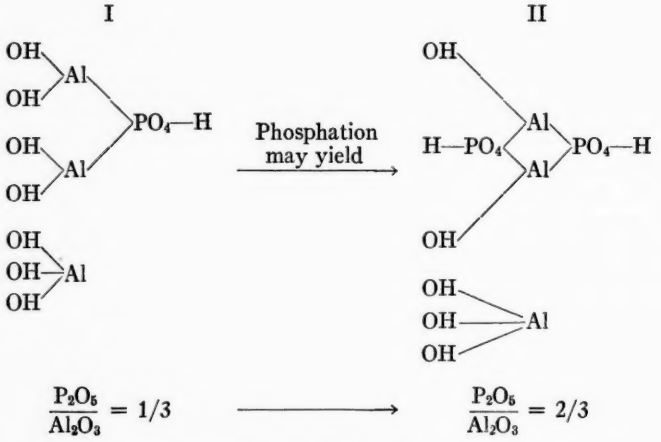
The ultimate pH value of the composite soil samples from cylinders receiving single, double, and triple amounts of phosphorus, may be compared to the field pH, total cation exchange, and exchange hydrogen. The drop in ultimate pH as the amount of added phosphate increases is well correlated with the corresponding increase in total cation exchange and exchange hydrogen.

These facts, especially the drop in ultimate pH value, further support Mattson's (16) contention that phosphates alter the acidoid-basoid ratio by increasing it, and as a result increase the total cation exchange capacity. Mattson has further shown that silicates and humates as well as phosphates act as acidoids (14), and any change in the amount of such substances effect a change in the acidoid-basoid ratio.

$$\frac{SiO_2,\ \text{humus},\ P_2O_5}{R_2O_3} = \frac{\text{acidoid}}{\text{basoid}}$$

It must be borne in mind, however, that the relation between the introduction of new acidoid constituents into the soil colloidal complex, and the increase in cation exchange capacity, is not a simple linear function. According to Mattson, the variations in the acidoid-basoid ratio express only one of several factors which greatly influence the behavior of the soil colloid.

The following structural formulas, taken from Mattson's studies, illustrate the alteration in the cation exchange capacity which may occur upon phosphation of a synthetic aluminum phosphate complex. Silicates or humates might enter the complexes in a similar way. No doubt soil colloids behave in a like manner.



In the case of complex number II the quantity of displaceable hydrogen is increased and displaceable hydroxyl ions decreased, indicating an increase in cation exchange capacity and a marked reduction in anion exchange capacity.

From these considerations the question may arise as to the influence of the organic matter content of these soils on the cation exchange capacity. It will be noted in the last column of table 1 that the organic matter content of the individual cylinders is rather uniform and shows no marked variation. Hence, in the case of these soils, the increase in total cation exchange capacity cannot be attributed to an increase in organic matter.

The individual cations, calcium, magnesium, potassium, and sodium, as determined by the ammonium acetate method, showed no difference in the amounts exchangeable when single, double, and triple amounts of phosphorus were added. Apparently it is only the amount of exchangeable hydrogen which is affected by increased phosphation on these soils. Further addition of alkali and alkaline earth cations to these soils would probably mean a greater adsorption by those soils receiving the most phosphates. With those soils where the pH was above 6.0, the exchangeable calcium and magnesium were greatest. The exchangeable potassium was very constant for all of the cyl-

inders, about 0.1 m.e. per 100 gm. of soil. Also the exchangeable sodium was very low, but it is interesting to note that the amount on the nitrate of soda treated cylinders was about twice as much as on the other cylinders. No exchangeable manganese was found on these soils.

INFLUENCE OF PHOSPHATION UPON THE CATION EXCHANGE CAPACITY OF A CALCIUM-SATURATED COLTS NECK LOAM

Evidence that phosphation of soil material increases the cation exchange capacity is further shown by the results of the laboratory experiment summarized in table 2. This work was carried out as follows: One hundred gram portions of a calcium-saturated Colts Neck loam soil were suspended in 500 cc. quantities of distilled water each containing increasing increments of P_2O_5 as di-sodium phosphate and allowed to stand overnight. The following

TABLE 2

Influence of phosphation upon the cation exchange capacity of a calcium-saturated Colts Neck loam

TREATMENT—P_2O_5 AS Na_2HPO_4	ANALYSIS OF SUPERNATANT LIQUID				ANALYSIS OF NH_4Cl EXTRACT		CATION EXCHANGE CAPACITY BY N NEUTRAL NH_4Cl	INCREASE IN CATION EXCHANGE CAPACITY	P_2O_5 HELD BY 100 GM. SOIL	IRON IN THE SOIL AS FREE Fe_2O_3
	pH	Humus	SiO_2	CaO	CaO	P_2O_5				
		mgm.	*mgm.*	*m.e.*	*m.e.*	*milli-moles*	*m.e. per 100 gm.*	*m.e. per 100 gm.*	*milli-moles*	*per cent*
Ca-soil*	6.95				15.38	trace	15.08			11.92
5 millimoles P_2O_5	8.05	150	2.5	0.61	15.08	0.5	18.12	2.95	2.9	11.56
15 millimoles P_2O_5	8.10	493	0.5	0.51	12.71	1.7	18.54	3.37	5.5	10.92
25 millimoles P_2O_5	8.15	583	3.0	0.48	10.80	2.3	19.39	4.22	7.3	9.97

* 1:2 water suspension.

day the supernatant liquid was filtered off and the soils were dried at a temperature between 50 and 60°C. The soils were then allowed to cool at room temperature. The cation exchange capacities of the soils were determined in triplicate on 10-gm. samples by the normal neutral ammonium chloride method. Total P_2O_5 determinations on the original calcium-saturated soil and on the phosphated calcium soils yielded the values for the quantity of P_2O_5 held by the soil. Free Fe_2O_3 was determined by the method of Drosdoff and Truog (7). Displaced organic matter in the supernatant liquid is expressed in terms of humus following the method of Tiurin (27).

An alteration in the nature of the exchange complex results upon phosphation and is evident from the data on the analysis of the supernatant liquid and the values for the cation exchange capacities as seen in table 2. Appreciable quantities of humus appeared in the supernatant liquid during phosphation, a fraction of which undoubtedly is due to increased solubility of the organic matter with increasing pH. The increase in humus cannot be entirely ascribed, however, to the forenamed effect, especially among the three phosphate

treatments, since in these cases a difference of only 0.1 pH unit exists in the three treatments and yet the data indicate a rise from 150 to 583 mgm. of humus in the supernatant liquid. The release of humus with increasing phosphation is in part due to a displacement of the humate fraction of the soil colloidal complex by phosphates (14). The low and irregular values for silica in the superantant liquid probably have no significance.

The quantities of phosphorus held by the soil include both a fraction loosely held by the soil and a fraction fixed by the free ferric oxides and possibly by exchanged calcium. It was to be expected, therefore, that the ammonium chloride treatment would extract some of the retained phosphorus. The data on the analysis of the ammonium chloride extract bears out this point; the extracted phosphorus values ranged from 0.5 to 2.3 millimoles of P_2O_5 from the lowest to the highest treatments of P_2O_5.

The exact behavior of the exchangeable calcium during phosphation cannot be followed with any degree of certainty from the data recorded in table 2. One point, however, is quite apparent, namely, that calcium is fixed during phosphation in the two higher phosphate treatments. This is illustrated by the displacement of only 12.71 and 10.80 m.e. of calcium oxide out of a total of 15.38 m.e. by the ammonium ion. The fixation of calcium may be due to the formation of calcium phosphate complexes (19). The behavior of the exchangeable calcium during the phosphation process is being further studied.

The retention of approximately 2.4 millimoles of P_2O_5 (millimoles P_2O_5 held minus millimoles P_2O_5 extracted by ammonium chloride) has increased the cation exchange capacity (at pH 7.0) by 2.95 m.e. Increasing retention of P_2O_5 has raised the cation exchange capacities by 3.37 and 4.21 m.e. with the two higher phosphate treatments. Undoubtedly, these recorded increases in the cation exchange capacity are not due entirely to phosphation, since an increase in pH generally increases this property (5). Nevertheless, the increase due to higher pH values must be compensated in part by the loss of humus, which has a high cation exchange capacity (a sample of humic acid prepared by one of the authors had a cation exchange capacity of 274 m.e. per 100 gm.). Whether or not the loss in exchange capacity due to the mobilization of organic matter exceeds the increase due to the rise in pH cannot be stated with certainty. The fact remains, however, that phosphation has increased the cation exchange capacity.

A parallelism between the increase in cation exchange capacity and a reduction in free ferric oxides is to be noted in the table. It is possible that new complexes of iron and phosphorus have been formed, and the increase in cation exchange capacity may be due in part to the exchange properties exhibited by these combinations.

SUMMARY

Base exchange studies were conducted on Sassafras silt loam soil which had received three different amounts of superphosphate yearly since 1922 and had received equivalent amounts of nitrogen from different sources.

Two extraction methods were used in determining the exchange hydrogen, the total cation exchange capacity, and the individual cations. Also several composite soil samples were electrodialyzed to determine the ultimate pH values.

The following important points were brought out by the analysis of these soils:

The field pH values were very little affected by increasing the amount of phosphates.

The exchangeable hydrogen was greatly increased by phosphation, and the ultimate pH values were lowered.

The total cation exchange capacity was distinctly increased when the phosphorus applications were doubled or tripled.

The above findings were very similar to those obtained by Merkle on the Pennsylvania Jordan field plots. They may be explained on the basis that phosphates increase the acidoid-basoid ratio. As a result, the total cation exchange capacity increases.

The exchangeable calcium, magnesium, potassium, and sodium showed no significant differences in relation to the amount of added phosphates.

Further evidence that phosphation of a soil material increases the cation exchange capacity was shown by a laboratory experiment using a calcium-saturated Colts Neck loam. With this soil, phosphation increased the cation exchange capacity depending upon the amount of phosphorus adsorbed. Also a correlation between the increase in cation exchange and the reduction in free ferric oxide was noted in this study.

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AVAILABILITY OF SOIL PHOSPHATES FOR THE PLANT FROM THE VIEWPOINT OF COLLOID CHEMISTRY

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In this paper the question of the availability of soil phosphates is considered from the standpoint of the chemistry of colloids, only the peculiar character of the fixation of phosphates in the soil, as a phenomenon of adsorption, and that of the "mobility" of the fixed phosphates, as the opposite phenomenon of "desorption,"[1] being taken into account. We know, of course, that the fixation of phosphates by soil and the opposite process, the so-called "mobility" of phosphates, may be considered from a purely chemical point of view, and so it is actually often dealt with in the literature.

If we consider the fixation of soluble phosphates, such as superphosphate and ammonium phosphate, from the colloid chemical viewpoint, the whole process should be explained in terms of adsorption of phosphate anions by soil gels. The task would be easier if the gels were uniform, for instance in their electrokinetic properties, within the limits of the same soil at least. The electrokinetic properties are mentioned because they are, as Mattson (15) and other authors, e.g., Gile (7), have demonstrated, very important for the adsorption of oppositely charged ions, but in reality there is no such uniformity in the the same soil or even in the same horizon. To the contrary, gels in one soil can be negative in one part and isoelectric in another (19, 21). The possibility is not to be excluded of the existence in soil of not only the two first groups of gels, but also of a third one, charged positively, as the existence of free sesquioxides in soil has been proved by a number of authors, e.g., Kerr (11), Ross (17), Denison (4). It is interesting to note, that Kubiena (12) was able to point out directly under the microscope both the motley character of soil colloids and the presence of areas of sesquioxides in this motley picture. Under the conditions of reaction commonly prevailing in soil (pH 7.0) the free sesquioxides will be charged positively.

Since the chief rôle in the fixation of soluble phosphates by soil is ascribed

[1] "Desorption" is the same thing as adsorption, only in "desorption" our attention is fixed on only those ions which, because of one or another adsorption process, pass into solution from the double layer. In other words, in some kinds of adsorption, while one ion enters the double layer and is fixed in it, another one is liberated from it. Such an ion, liberated from the double layer, we call a "desorbed ion," and the process itself, of the passage of the ion into solution, we name "desorption."

to the sesquioxides, our investigation began with a study of these. This was done in the work of Shtatnov and Odintzova in 1934 (18) under the guidance of the author.

The process of fixation of soluble phosphates in soil by means of adsorption—had been already demonstrated. We were interested in the opposite process, that of "desorption" under conditions of varying degrees of saturation of the iron gel by the phosphate anion. This phenomenon might have been studied either by displacing the phosphate anion by other anions under varying conditions, as was done by Demolon and Bastisse (3), or directly in the plant under given conditions. We chose this second method.

A freshly prepared iron gel was saturated to different degrees with phosphate anions from solutions of varying concentrations of monosodium phosphate (NaH_2PO_4). The availability of these adsorbed phosphate anions to the plant (oats) was then tested directly, all other conditions being equal. The technique used for saturation is very important in this case. The aim is to get uniform distribution, and the following procedure was adopted: Large volumes of solutions of varying concentration of NaH_2PO_4 were prepared in large glass cylinders. Iron gel (or soil) was then poured into the solution and carefully mixed. When the entire gel had settled and the solution over the precipitate had become clear, the solution was pound off and the gel transferred into a parchment sack for dialysis. After dialyzation, the gel was dried at 30°C. and tested for P_2O_5.

The results of the analyses are summarized in table 1. As may be seen from this table, three degrees of saturation were obtained. The strongest solution produced a lower degree of saturation than the medium one. We are unable to give a full explanation of this phenomenon; we can offer only a theory. The electrokinetic properties, determined by a rough qualitative test (by means of electrophoresis), proved different in all three cases. The iron gel in the lower degree of saturation remained positively charged; after saturation from the 0.1 *M* phosphate solution it became isoelectric, and after saturation from the strongest solution —0.25 *M*—it became negatively charged. It is possible that the high content of adsorbed phosphate anions after saturation from the 0.1 *M* solution is somehow related to the isoelectric condition of the gel.

The material which was to serve as the source of phosphate nutrition for the plants was supplied in an isolated state, not as a part of some general nutrient mixture. The inner container into which one part of the roots was placed was filled with Helriegel's nutrient mixture but without phosphates, whereas the outer container, into which the remaining roots were put, contained only phosphates mixed with pure quartz sand. With this arrangement, only the organic anions liberated by the plant itself would displace the phosphate anion from the double layer. In other words, we feared that other anions of the nutrient mixture might increase the availability of the adsorbed phosphate anions to the plant. It appeared in the course of this investigation, however, that these fears were groundless. In those cases where the solution from the inner con-

tainer passed into the external one, the phosphate anions at a low degree of saturation were also unavailable to the plant, in whatever amount they were supplied.

Table 2 shows the results of the experiments with the iron gel. The availability of the adsorbed phosphate anions, under the conditions of our experiment, increases with the degree of saturation of the gel. Moreover, below a certain degree of saturation, the phosphate anion is totally unavailable to the plant, whatever the amount applied. We have called the degree of saturation below which the adsorbed anions remain unavailable to the plant the "critical zone of saturation." Its great practical significance was pointed out. A

TABLE 1

Analyses of dialyzed phosphate gels

GEL NUMBER	CONCENTRATION OF NaH_2PO_4 SOLUTION	RATIO OF SOLUTION TO GEL	P_2O_5 ABSORBED PER GM. OF GEL	pH OF SUPERNATANT LIQUID (MICHAELIS METHOD)	pH OF RESPECTIVE NaH_2PO_4 SOLUTION
	M		*mgm.*		
1	0.25	300:1	16.72	5.1	4.5
2	0.1	300:1	21.12	5.9	4.8
3	0.001	500:1	3.23	7.0	5.5

TABLE 2

Yield of dry matter with variously saturated gels

(gm. per container)

P_2O_5 PER CONTAINER	FREE NaH_2PO_4	P_2O_5 FIXED BY IRON GEL (MGM. P_2O_5 PER GM. OF GEL)		
		3.238	16.726	21.12
mgm.	*mgm.*			
10	5.34	3.51	3.75	3.68
30	9.51	4.06	5.67	6.28
80	18.51	3.22	10.38	15.80
160	20.74	5.89	17.24	....

knowledge of the phenomenon of the "critical zone of saturation" may permit the computation of the quantity of fertilizer to be added to the soil in question. The particular significance of this was pointed out in an earlier paper (20).

In 1935 the Soil Colloid Laboratory of the All-Union Institute of Fertilizers inaugurated experiments directly on soil, instead of, as first planned, on the availability of adsorbed phosphate anions from soil gels with varying electrokinetic properties. S. V. Odintzova and A. N. Lawrienko worked on pot-culture experiments on krasnozem (red soil), and E. M. Rosenfeld, on chernozem from which Ca had been removed. The soils were, however, so selected as to reflect to a certain degree the original plan: krasnozem was to imitate gels of the sesquioxide type which we already had studied in pure condition, and

chernozem was to imitate negatively charged gels. To avoid complications which might be caused by the calcium cation, we eliminated it from chernozem by the method proposed by Gedroitz, i.e., by treatment with 0.05 *N* HCl and subsequent neutralization with weak solutions of sodium hydroxide.

TABLE 3

Analytical results on soil experiments

SOILS	RATIO OF SOLUTION TO SOIL	CONCENTRATION OF NaH_2PO_4 SOLUTION	P_2O_5 CONTENT PER GM. OF SOIL
		M	*mgm.*
Original soil	.....	....	1.18
Saturated	200:1	0.01	16.0
Saturated	200:1	0.25	25.93

TABLE 4

Crop yields on krasnozem

(gm. per container)

P_2O_5 PER CONTAINER	DRY MATTER ON ORIGINAL SOIL: 1.18 MGM. P_2O_5 PER GM. OF SOIL	P_2O_5 PER CONTAINER	DRY MATTER ON	
			First degree of saturation: 16.0 mgm. P_2O_5 per gm. of soil	Second degree of saturation: 25.93 mgm. P_2O_5 per gm. of soil
mgm.	*gm.*	*mgm.*	*gm.*	*gm.*
5	3.22	10	3.59	7.0
15	2.98	30	5.05	7.37
25	3.15	50	9.36	9.77
40	2.86	80	12.72	12.80
75	2.95	150	12.70	16.22

TABLE 5

Crop yields on chernozem

(75 mgm. P_2O_5 per container)

DEGREE OF SATURATION OF CHERNOZEM	AVERAGE YIELD PER CONTAINER
	gm.
Original soil, 1.6 mgm. P_2O_5 per gm. of soil	3.06
Ca-free soil, 0.49 mgm. P_2O_5 per gm. of soil	3.15
Ca-free soil, saturated 2.4 mgm. P_2O_5 per gm. of soil	6.33
Ca-free soil, saturated 3.54 mgm. P_2O_5 per gm. of soil	9.33

The krasnozem was brought from a tea plantation in one of the humid subtropical districts of U.S.S.R. (Chakva, sample taken from fallow land overgrown by ferns). The soil was screened through a 0.25-mm. sieve and then placed into large cylindric containers (40 l.) filled with solutions of the same phosphate (NaH_2PO_4) in varying concentrations. After this it was continu-

ously and carefully mixed for 2 days to issue uniform saturation. The rest of the procedure was the same as in the experiments with the iron gels: pouring off of the supernatant liquid after sedimentation, dialization of sediment, and testing for P_2O_5.

The results are summarized in table 3. As this table shows, two different degrees of saturation were obtained.

From 5 to 150 mgm. of P_2O_5 were then introduced into the external container, with the results shown in table 4. As was observed in experiments with the iron gel, here also the higher is the degree of saturation of krasnozem, the higher will be the availability of the adsorbed phosphate ions. There is also a critical zone, which, however, we did not try to determine more precisely in this case. It is clear only that the degree of saturation of the original soil with phosphate anions lies below this critical zone.

In Rosenfeld's experiment with the Ca-free chernozem, the original chernozem contained 1.6 mgm. P_2O_5 per gram of soil; after removal of Ca, the chernozem contained only 0.49 mgm. P_2O_5. Saturation from a 0.005 *M* solution, using 50 volumes of the solution to 1 volume of soil, raised the content of P_2O_5 to 2.4 mgm. per gram of soil, and from the 0.01 *M* solution, to 3.54 mgm. It must be noted that saturation of chernozem from higher concentrations than 0.01 *M* did not increase the degree of saturation; on the contrary, the curve of saturation turned downward. The causes of this phenomenon were not investigated.

The results of the experiment with chernozem are summarized in table 5. As can be seen, here also there is a critical zone of saturation, below which the phosphate anions are unavailable and above which they are available, the degree of availability rising with the degree of saturation.

Parallel with the application of 75 mgm. P_2O_5 per container, an application of 125 mgm. P_2O_5 per container was tested. The results obtained were the same: at the low degree of saturation, the larger application of P_2O_5 remained as unavailable to the plant as the smaller one, and above the critical zone, the yield increase was proportional to the degree of saturation.

DISCUSSION

In the experiment for the determination of the availability of adsorbed phosphate anions to the plant, if careful precautions are taken to obtain uniform saturation of the iron gel or soil, an evident dependence of this availability on the degree of saturation of the gel or soil with the phosphate anions is observed. This has been demonstrated by our experiments; was predicted earlier on theoretical grounds by Gaarder (6), Demolon and Barbier (2) et al.[2]; and later was indicated also by Hibbard (9). It is still not clear, however, with what type of adsorption we are dealing. On the basis of recent work, three

[2] Gordon seems to be the first to have done work in this direction on plants. We did not have access, however, to his work in the original (WILEY, R. C., AND GORDON, N. E. 1923 Availability of adsorbed phosphates. *Soil Sci.* 15: 371–373).

types of absorption may be distinguished, as indicated by Verwey (22): (*a*) adsorption according to Gibbs; (*b*) exchange of counter-ions (the ionic spheres of opposite charge around the colloid-ions—charged particles); (*c*) assimilation of potential-determining electrolytes.

The first type of adsorption has but limited importance for electrolytes in soil.

The second type—exchange of counter-ions—is very important in soil for the cation exchange in negatively charged gels. As for anions, this kind of adsorption is applicable only to positively charged gels. Our experiments show, however, that phosphate anions are least available for the plant when the iron gel retains its positive charge. Only after the iron gel has passed into the isoelectric condition, particularly on the negative side, do the adsorbed phosphate anions become available to the plant. Hence the necessity follows of grounding theoretically the desorption of phosphate anions from the isoelectric or electronegative soil gels.

The adsorption of phosphate anions might be explained with the aid of the assimilation of potential-determining electrolytes. In this case one of the ions is included in the crystal lattice and it determines the sign of the colloid charge and the potential. The phosphate anion would charge the isoelectric colloid negatively. The other ion, in our case the cation, would occupy its place in the external layer. But such an assumption makes it difficult to understand the opposite process, that of the desorption of phosphate anions. Indeed, to make it possible for the negative ion to break through the surface of the crystal lattice, which is also negatively charged, it must possess not only corresponding dimensions, but also a very high energy of activation. Even some of the phosphate anions satisfy these conditions, they do not suffice for the desorption of the said ions. For the desorption of phosphate anions it is necessary that other anions, e.g., the anions of organic acids, satisfy these conditions. Only under these circumstances would the phosphate anions be able to pass from the crystal lattice into the surrounding solution and become available to the plant. But such an assumption is improbable. It seems more expedient, therefore, to accept for the explanation of the desorption of phosphate anions from negatively charged gels the theoretical considerations of Kargin concerning molecular adsorption. Kargin in his reports[3] on molecular adsorption has demonstrated that purified ammosilicates adsorbed both ions of the electrolyte from the solution in equivalent quantities. If, after this, electrolytes are introduced into the solution, a new equilibrium is established, the result of which will be adsorptional distribution. This means that the ions of the new electrolyte will enter the double layer in pairs, and from it a part of the adsorbed phosphate anions will pass into the solution. Kargin has shown, besides, that the lower the solubility of the respective salt, the higher the molecular adsorption (in the case of silver salts). It is probable that this rule will hold true also in respect of phosphates of various solubilities.

[3] Unpublished.

From the work of Kargin, it is possible to explain both adsorption and desorption of phosphate anions without resorting to the phenomenon of penetration of these ions into the crystal lattice of negatively charged soil colloids. Both adsorption and desorption of phosphate anions will take place in the double electric layer of the negatively charged gels at the surface of the colloid particle. This does not mean that molecules, as such, are adsorbed in this process. Adsorption in the ion form is more probable. At first, as a result of affinity and high energy of activation, a certain quantity of phosphate anions, in spite of the force of repulsion exerted by the negative colloid on the anion, will enter the double layer and approach definite areas of the crystal lattice. But then the electric properties of the double layer will suffer an alteration: the electrokinetic potential will be raised. This will lead to the entering of equivalent amounts of cations from the solution, and adsorption will become molecular. This is the manner in which adsorption of phosphate anions would proceed, according to Kargin. When new electrolytes, such as organic acids, are introduced into the solution, the anions of these acids and their respective cations will enter the double layer in the manner already described. But since this double layer is already saturated, the phosphate anions, together with a part of the cations, will pass into solution. This will be desorption, as the result of adsorptional distribution of ions.

The results of Mattson (16) on the displacement of silica anions from negatively charged colloids with the help of, or by means of, phosphate anions, as well as the results of the experiments of Demolon and Bastisse (3) on the displacement of phosphate anions from soils by the anions of various acids, can also be explained from this standpoint.

Future work on this problem may well be developed along one of the following lines.

Our idea that each soil possesses its own critical zone of saturation might be used for determining quantitatively, at least approximately, the fertilizer requirement of the soil, particularly in regard to phosphates. This method is preferable to the cumbersome pot-culture method. A method must be elaborated for the determination of the limit of the degree of saturation, which may be called provisionally "the soil absorption capacity," with respect to phosphate anions. Of course, this value should be determined only under definite conditions of pH, of concentration, of ratio of soil to the amount of the salt solution, and of time of contact. But this will not impair its practical value.

Many attempts have been made to determine the reserves in the soil of phosphoric acid available to the plant (2, 5, 8, 9, 13, 14, 22) but they were concerned mostly with solubility. Of these, the most pertinent to our work is that of Demolon et Barbier (2). Particularly valuable are the results they obtained with citrates, though the authors themselves are not certain about their method. They say that more phosphoric acid passes into the citrate solution than into that of acetic and nitric acid, because the citrate destroys

the adsorbents in the soil. Lohse and Ruhnke seem to us to be nearer the truth when they indicate (13, p. 450) that such acids as acetic and nitric liberate not only the phosphoric acid but also other ions, such as that of iron, and the latter precipitates the phosphate anion. This is eliminated in citrate treatment, as here a complex compound is formed. In short, we think that the citrate method of Demolon et Barbier might supply interesting results if it were modified and adapted to the aims we are pursuing.

It is possible that microbiologic methods might prove both easier and more suitable for determining the availability of phosphoric acid to the plant, but this is outside the realm of this treatise.

It was not our intention to deal here with the problem of the means of lowering the level of the critical zone of saturation, which is of great practical importance. Such a lowering may be achieved, however, by means of liming or introduction of silica, as has been indicated by Gaarder (6, p. 41), or by the introduction of organic fertilizers. This subject will be dealt with in a special article.

SUMMARY

An attempt has been made to study the availability of adsorbed phosphate anions to the plant from the standpoint of colloidal chemistry.

The gel of iron and two soils—krasnozem and chernozem—were used as absorbents.

Both the iron gel and the soils were evenly saturated with phosphate anions to varying degrees of saturation by means of a special method.

The direct availability of the adsorbed phosphate anions to the plant (oats) was tested in pot-culture experiments (with isolated nutrition) in relation to the degree of saturation.

The phosphate anions became available to the plant at the critical zone of saturation. Below this zone the phosphate anions are unavailable to the plant, even when supplied in quantities for exceeding the needs of the plant.

In explaining the availability or desorption of phosphate anions we have mainly utilized the theoretical considerations of Kargin, which follow from his recent, unpublished work on molecular adsorption and adsorptional distribution.

The practical significance of the critical zone of saturation for the quantitative determination of the fertilizer requirement of the soil is indicated.

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PHYSIOLOGICAL STUDIES ON RHIZOBIUM: VII. SOME PHYSIOLOGICAL EFFECTS OF ACCESSORY GROWTH FACTORS[1]

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In a previous paper of this series (7) it was shown that the rhizobia are able to grow continuously with frequent transfers in properly balanced media made up of c.p. materials. No evidence was found that these organisms require any complex unidentified substances for either growth or respiration. Allison and Hoover (1, 2, 5), however, have shown that certain extracts greatly facilitate the growth of the rhizobia in a synthetic (mineral-nitrate-sucrose) medium. The accessory substances in these extracts were found also to stimulate the growth and oxygen utilization of these organisms in similar media containing nitrogen sources other than nitrates.

Allyn and Baldwin (3, 4) showed that some reducing agents such as cysteine and thioglycollic acid in certain concentrations greatly increased the growth of the rhizobia in a mineral-nitrate-mannitol medium. Thorne and Walker (7) found that cysteine induced increases in the growth and respiration of the rhizobia comparable to those brought about by brown cane sugar which contains appreciable quantities of accessory factors. Such results seemed to suggest that the explanation of the ability of the accessory growth substances studied to stimulate these organisms might be associated with a reducing effect, tending to bring about a more favorable potential in the medium for growth. The present investigation was planned to study some of the physiological effects of these stimulative materials upon the rhizobia.

PROCEDURE

It has been found very convenient to study the influence of the various stimulative substances upon the rhizobia by the determination of the gaseous exchange of the organisms in the presence of these materials. The net oxidative and reductive changes of organisms can be conveniently expressed by their respiratory quotients. The respiratory quotient is the value obtained from the ratio,

$$\frac{\text{Volume } CO_2 \text{ produced}}{\text{Volume } O_2 \text{ consumed}}$$

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In general the respiratory quotient of bacteria seems to be influenced by two major factors: first, the chemical composition and physical characteristics of the medium in which the organisms are grown, and, second, the natural or innate oxidation-reduction characteristics of the organisms.

Oxygen consumption and CO_2 production of the rhizobia were determined with Warburg manometers according to the direct method of Warburg (8). A special absorption coefficient for CO_2 was determined for the medium used under the pressure range encountered in the various studies. This coefficient was substituted in Warburg's equation and used in calculating the CO_2 vessel constant for each of the respirometer vessels used without alkali in the inner well. Although this method is not applicable to all microörganisms, a number of experiments have shown it to be very accurate for the rhizobia. It has the advantage that continuous readings of both oxygen and CO_2 can be made, whereas, with other methods CO_2 production is determined only at the end of the experiment. The method is adaptable to these organisms because of their aerobic nature and also because they bring about no appreciable change in the pH of the medium during such short periods as those in which the determinations were made.

The following basal medium was employed throughout the experiments reported: K_2HPO_4, 0.5 gm.; $MgSO_4 \cdot 7H_2O$, 0.2 gm.; NaCl, 0.1 gm.; $CaCO_3$, 3.0 gm.; $FeCl_3$, 0.01 gm.; distilled water, 1,000 cc. The sugars employed were added to give a concentration of 1 per cent; the fixed nitrogen content of each medium was made up to 100 p.p.m. The preparation of inocula and the procedure with the Warburg respirometers were the same as in the previous work (6, 7).

Strain 206 of *Rh. trifolii* and 132 of *Rh. meliloti* of the laboratory stock cultures were used for the various studies. Most of the data reported are for *Rh. trifolii*, similar results were also obtained with cultures of the alfalfa organisms.

EXPERIMENTAL

In the first experiments of this series the organisms used for inoculum were prepared by culturing in yeast extract medium. The media employed in the tests and the oxygen consumption and respiratory quotients of the cultures of *Rh. trifolii* during 16 consecutive hourly intervals are given in table 1.

The data of table 1 show that cysteine, soil extract, brown cane sugar, alfalfa extract, and yeast extract each led to a distinct reduction in the value of the respiratory quotient of the organisms when compared to the quotient of the control culture growing in the KNO_3-sucrose c.p. medium. The respiratory quotients of the cultures in the media to which cysteine, soil extract, or brown cane sugar had been added increased rapidly after growth of the organisms had begun. It seems probable from these results that the stimulative substances studied contain materials acting as reducing agents or initial hydrogen donators for the organisms. The reducing substances contained in

these materials were apparently rapidly utilized. This was indicated by the comparatively short time in which the values of the respiratory quotients of the cultures in the presence of these substances rose to about the same value as that of the respiratory quotient of the control culture. Yeast extract and alfalfa extract were present in greater concentrations than the other accessory factors and also exerted a reducing effect upon the quotient over a longer period

TABLE 1

Oxygen consumption and respiratory quotients of Rh. trifolii during consecutive hourly intervals in media containing different substances

Organisms for inoculum cultured in yeast extract medium

KNO_3* + sucrose c.p.						KNO_3* + brown cane sugar		Alfalfa extract* no. 4 + sucrose c.p.		Yeast extract* + sucrose c.p.	
Control		Cysteine†		Soil extract‡							
O_2	R.Q.	O_2	R.Q.	O_2	R.Q.	O_2	R.Q.	O_2	R.Q.	O_2	R.Q.
cu. mm.		*cu. mm.*		*cu. mm.*		*cu. mm.*		*cu. mm.*		*cu. mm.*	
20.9	1.04	18.1	0.95	37.2	0.77	33.3	0.84	39.6	0.78	37.7	0.64
33.5	1.09	45.5	0.87	66.2	0.83	52.5	0.85	90.9	0.77	85.8	0.85
37.4	1.08	62.7	1.01	62.8	0.92	54.4	0.94	105.5	0.83	103.8	0.90
40.2	1.13	74.3	1.04	55.8	0.96	58.9	1.01	116.1	0.86	102.4	1.03
43.6	1.13	83.7	1.07	58.3	0.93	73.1	1.08	110.6	0.92	117.2	0.97
48.2	1.12	88.5	1.03	59.4	0.98	87.2	1.15	130.6	0.91	134.7	0.95
42.8	1.16	89.4	1.05	58.6	1.02	90.2	1.15	112.6	0.92	110.0	0.99
43.8	1.13	85.5	1.02	57.1	1.04	85.5	1.16	109.6	0.93	94.1	1.02
45.9	1.08	97.1	1.05	61.1	1.00	97.7	1.15	104.9	0.93	95.4	0.97
50.3	1.10	108.5	1.08	64.5	1.04	112.7	1.15	80.7	0.97	93.8	0.99
47.7	1.11	116.4	1.08	61.4	1.08	121.5	1.15	72.6	0.94	85.9	1.01
50.1	1.13	120.8	1.13	63.0	1.12	132.0	1.17	71.5	0.92	80.5	1.04
52.4	1.10	133.4	1.10	68.2	1.07	148.7	1.16	67.7	0.98	85.7	1.00
53.0	1.10	119.7	1.16	63.3	1.11	155.2	1.23	67.5	0.94	77.3	1.02
51.0	1.14	101.3	1.18	72.1	1.12	151.8	1.21	63.5	0.94	76.9	1.02
55.4	1.10	84.4	1.22	74.1	1.11	132.5	1.20	59.1	1.01	71.2	1.02
716.2	1.11	1,429.3	1.08	983.1	1.02	1,587.2	1.14	1,403.0	0.92	1,452.4	0.97

* KNO_3, alfalfa extract, and yeast extract in concentration of 100 p.p.m. of N.

† Cysteine 0.002 per cent.

‡ Soil extract 1 gm./liter.

of time than was observed for the other materials. Yeast and alfalfa extracts are composed largely of protein materials having theoretical respiratory quotients near 0.80, and are also readily available nutrient sources for the rhizobia. The low respiratory quotients of *Rh. trifolii* in media containing these proteinaceous extracts might, therefore, be explained as due to the organisms oxidizing considerable of these materials, which are more reduced than sugars, for their source of nutrition and energy.

An investigation similar to that reported in table 1 was conducted using inocula freed from growth substances by culturing the organisms for several transfers in KNO_3-cane sugar medium. An alcoholic extract of *Az. vinelandii* medium, prepared according to the method of Hoover and Allison (5) was investigated in addition to the materials studied in the previous experiment.

TABLE 2

Oxygen consumption and respiratory quotients of Rh. trifolii during consecutive hourly intervals in media containing different substances

Organisms for inoculum cultured in KNO_3 medium

KNO_3* + SUCROSE C.P.								KNO_3* + BROWN CANE SUGAR		ALFALFA EXTRACT* NO. 4 + SUCROSE C.P.		YEAST EXTRACT* + SUCROSE C.P.	
Control		Cysteine†		Soil extract†		Az. vin. extract‡							
O_2	R.Q.	O_2	R.Q.	O_2	R.Q.	O_2	R.Q.	O_2	R.Q.	O_2	R.Q	O_2	R.Q.
cu. mm.		*cu. mm.*		*cu. mm.*		*cu. mm.*		*cu. mm.*		*cu. mm.*		*cu. mm.*	
8.0	1.24	8.5	0.89	13.7	0.83	5.2	0.95	11.6	1.01	13.1	1.00	15.6	0.90
8.4	1.13	8.5	0.75	17.4	0.83	9.3	0.90	12.7	1.04	17.3	0.92	13.8	0.88
9.2	1.12	8.8	0.78	23.6	0.84	13.7	0.84	15.9	1.01	22.1	0.95	23.4	0.86
7.3	1.10	9.0	0.85	24.2	0.87	14.6	0.90	18.7	1.04	28.3	0.95	26.9	0.91
6.9	1.11	9.6	0.86	24.5	0.93	13.1	0.82	18.7	1.08	29.2	0.94	32.9	0.91
7.1	1.05	10.0	0.92	26.7	0.94	11.7	0.95	20.1	1.10	35.6	0.93	43.5	0.98
6.3	1.10	10.9	0.96	27.9	0.93	11.1	0.93	21.8	1.10	32.2	0.94	45.9	0.98
7.1	1.10	10.6	0.98	28.2	0.96	11.6	0.93	24.9	1.07	45.1	0.92	54.5	0.93
7.1	1.06	10.5	0.95	31.3	0.96	11.4	0.96	29.7	1.10	50.7	0.91	61.0	0.91
6.4	1.08	10.5	0.94	31.3	0.96	11.9	0.95	34.6	1.15	55.7	0.90	65.0	0.89
5.1	1.07	10.3	0.95	31.3	0.96	10.6	0.94	36.8	1.17	57.0	0.87	65.6	0.88
4.5	1.10	10.0	1.03	33.6	0.96	10.1	0.98	40.5	1.18	58.6	0.88	66.2	0.87
4.3	1.09	10.1	1.04	34.1	0.97	10.1	1.00	46.4	1.21	69.2	0.87	70.3	0.87
5.1	1.08	10.3	0.98	35.6	0.98	9.3	0.96	51.3	1.20	68.4	0.87	74.6	0.87
5.3	1.10	9.9	0.96	36.9	0.92	9.6	1.01	51.5	1.20	70.6	0.89	71.0	0.89
4.3	1.09	9.3	0.95	33.2	0.91	7.5	1.07	57.8	1.15	77.9	0.91	70.8	0.88
102.4	1.12	156.8	0.95	453.5	0.93	170.8	0.93	493.0	1.15	731.0	0.90	801.0	0.90

* Concentration of 100 p.p.m. N.

† Concentration of 0.004 per cent.

‡ Concentration of 1 gm./liter.

The oxygen consumption and respiratory quotient of *Rh. trifolii* in the different media are shown in table 2.

The respiratory quotients of these cultures were slightly different in some cases from the quotients given in table 1, but the same general changes with time were observed. The somewhat greater variability in respiratory quotient values in this experiment, as shown in table 2, in comparison with the quotients shown in table 1 can be largely accounted for by reason of the lower rate of

respiration of the cultures from which the data of table 2 were obtained. The influence of the *Az. vinelandii* medium extract resembled that of the other accessory materials in that it brought about a distinct lowering of the respiratory quotient of the organisms for some time after inoculation.

Another experiment was conducted in which the organisms employed for the inoculation had been cultured for several transfers in NH_4Cl-cane sugar medium. The influence of the various non-nitrogenous factors upon the

TABLE 3

Oxygen consumption and respiratory quotients of Rh. trifolii during consecutive hourly intervals in media containing different substances

Organisms for inoculum cultured in NH_4Cl medium

NH_4Cl* + SUCROSE C.P.						NH_4Cl* + BROWN CANE SUGAR		YEAST EXTRACT* + SUCROSE C.P.	
Control		Cysteine†		Soil extract‡					
O_2	R.Q.	O_2	R.Q.	O_2	R.Q.	O_2	R.Q.	O_2	R.Q.
cu. mm.		*cu. mm.*		*cu. mm.*		*cu. mm.*		*cu. mm.*	
10.0	1.08	9.8	0.78	17.7	1.00	13.2	0.84	19.8	0.88
10.0	1.10	10.2	0.89	22.3	1.05	17.5	0.91	21.4	0.97
11.4	1.26	11.5	0.91	28.0	1.18	20.4	1.07	29.9	0.98
11.2	1.34	11.3	0.89	33.2	1.16	24.9	1.08	33.2	0.97
13.4	1.28	14.8	1.06	39.6	1.14	32.8	1.10	34.5	0.95
15.7	1.28	15.9	1.17	45.7	1.19	39.9	1.21	45.0	0.99
17.5	1.28	22.8	1.13	48.0	1.25	54.0	1.22	52.6	1.03
22.8	1.18	29.8	1.13	60.4	1.21	74.6	1.04	58.4	1.03
28.3	1.18	39.4	1.20	73.1	1.20	103.0	1.08	62.0	1.03
33.4	1.15	51.5	1.22	78.0	1.15	114.6	1.13	62.0	1.01
34.2	1.21	59.9	1.20	80.4	1.11	148.8	1.18	71.6	1.00
37.6	1.26	77.3	1.20	96.1	1.14	169.0	1.17	75.9	0.96
44.5	1.20	102.0	1.18	110.0	1.13	187.0	1.17	77.0	0.90
40.7	1.22	102.0	1.19	118.8	1.09	185.0	1.17	75.2	0.91
330.7	1.21	558.2	1.16	851.3	1.15	1,184.7	1.14	718.5	0.97

* Concentration of 100 p.p.m. N.

† Concentration of 0 002 per cent.

‡ Concentration of 1 gm./liter.

respiration of *Rh. trifolii* was tested with NH_4Cl as the nitrogen source. The oxygen consumption and respiratory quotients for the organisms growing in the different media are given for 14 consecutive hourly intervals in table 3.

The data of table 3 show changes in the respiratory quotients of the various cultures which were similar to those observed in the previous test. The initial reduction of the quotients was, in general, not so large as for the cultures reported in tables 1 and 2 where KNO_3 was employed as the nitrogen source.

The data in tables 1, 2, and 3 show the stimulative effect of the different

extracts upon oxygen consumption by *Rh. trifolii*. One difference between the data in the three tables is that the organisms which had been cultured in yeast extract medium previous to inoculation responded to the addition of cysteine to a much greater extent than did the organisms which had been growing in either the KNO_3 or NH_4Cl media. This might indicate that the organisms grown in the KNO_3 and NH_4Cl media had become somewhat adapted to a higher potential than those grown in yeast extract medium. On the other hand, the stimulation might be explained by the fact that the organisms grown in the yeast extract medium are able to carry appreciable quantities of accessory growth substances within their cells. This would enable them to respond to a greater extent to an improved potential of the medium than would be possible for organisms which had been largely freed from such factors. It seems probable that the differences in response to cysteine might be a result of a combination of the two causes suggested.

The data reported here entirely agree in that each factor which induced an increase in the rate of oxygen consumption by *Rh. trifolii* also brought about an initial decrease in the values of the respiratory quotients. It is not claimed that the reducing action of these substances is the complete explanation of their beneficial influence upon the rhizobia, but this effect does seem to be at least one of their important functions.

EFFECT OF AGAR UPON RESPIRATORY QUOTIENTS

The influence of the various stimulative extracts upon the nodule bacteria seemed to be related to some of the effects noted for agar. Allison and Hoover (1) found a higher growth rate of the rhizobia in KNO_3-sucrose c.p. medium when agar was present. They suggested that the stimulation brought about by agar was due to accessory growth substances present in the agar. Allyn and Baldwin (4) observed that agar facilitated the growth of the rhizobia in a KNO_3-mannitol medium. They also found that agar reduced the oxidation-reduction potential of the medium as much as 100 millivolts. From their studies it was concluded that the beneficial effects of agar upon the organisms could be satisfactorily explained by the change brought about in the potential of the medium. Although the studies of these different workers are not directly comparable, the differences in the explanations offered for the stimulative effects of agar seemed to merit further study.

A study was made, therefore, of the influence of agar upon oxygen consumption and the respiratory quotient of *Rh. meliloti*. Sodium nitrate and yeast extract were used as sources of nitrogen in concentrations of 100 p.p.m. of nitrogen. Glucose was the sugar used. Agar was added to the media at the rate of 15 gm. per liter. Two cubic centimeters of medium were placed in each manometer vessel. The vessels were allowed to stand long enough for the agar medium to solidify before inoculations were made. To each manometer flask, containing 2 cc. of medium, there was added 0.2 cc. of a suspension of *Rh. meliloti* which had been cultured free of accessory growth substances.

In the first experiment with agar, $NaNO_3$ (100 p.p.m. of nitrogen) was used as the nitrogen source in the medium. Both oxygen consumption and CO_2 production were determined for the various cultures. The oxygen consumption of the duplicate cultures was plotted against time. The resulting curves are given in figure 1.

The data in figure 1 indicate that in the absence of glucose the organisms were able to utilize only a very small fraction of the agar. In the presence of glucose, agar brought about a considerable increase in the rate of oxygen utilization. When yeast extract was substituted for $NaNO_3$ in a similar set of experiments no such stimulative effects were noted from the agar. It seems evident, therefore, that agar did not improve the yeast extract medium with respect to oxygen utilization by the organisms and that agar produced no beneficial effects upon *Rh. meliloti* that were not also produced by yeast extract.

In the presence of yeast extract, agar brought about no appreciable change in the respiratory quotients of the organisms. The bacteria growing on the agar-nitrate medium, however, had respiratory quotients quite different from those in the nitrate medium without agar. The respiratory quotients obtained in the same experiment as the data from which the curves in figure 1 were taken were plotted against time. The resulting curves are shown in figure 2.

Although the cultures in the presence of agar had a higher respiratory quotient for the first 2-hour interval the quotients decreased rapidly and continuously as growth continued. It seems probable that the organisms first utilized the liquid medium which separates from agar as it cools and so were not influenced appreciably by the agar during the first 2-hour interval. The lowering of the quotients as the growth of the organisms continued might be interpreted as resulting from the organisms' coming into more direct contact with the agar as the nutrients in the liquid medium were exhausted. Such a lowering of the respiratory quotients by agar is in harmony with the observation of Allyn and Baldwin that it brings about a lower potential of the medium.

The study of agar seems to indicate that the beneficial effect it exerts upon the rhizobia can be accounted for to only a very minor extent by the nutrient materials which it contains. Since it has been shown that agar reduces the oxidation-reduction potential of a nitrate medium and the present investigation indicates that it brings about a significant decrease in the respiratory quotients of the organisms, it seems probable that the reducing effect of the agar is, at least, one of the important reasons for the stimulative effect it exerts upon the rhizobia.

Attempts were made to measure the oxidation-reduction potential of different media under aerobic conditions with an electron tube potentiometer, but the results obtained were not very satisfactory. Indications were obtained, however, that the substances which stimulated the growth and oxygen utilization of the rhizobia and which lowered the respiratory quotient of the organisms also reduced the oxidation-reduction potential of KNO_3-sucrose c.p. media.

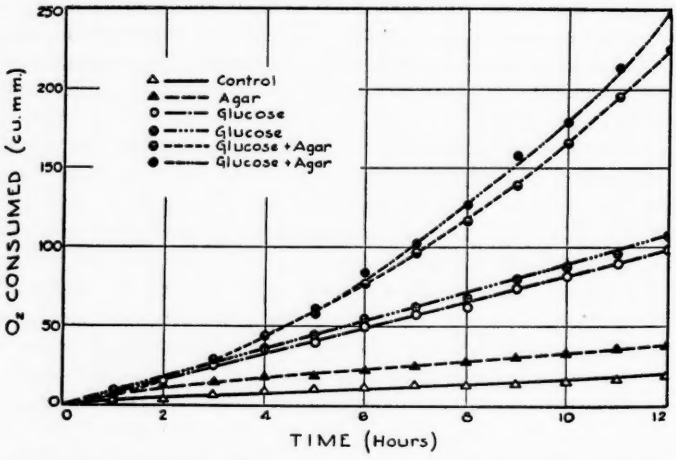

FIG. 1. OXYGEN CONSUMED BY RHIZOBIUM MELILOTI IN A NITRATE-MEDIUM WITH AND WITHOUT GLUCOSE AND AGAR PRESENT

Inoculum freed of accessory growth substances by culturing in KNO_3-cane sugar medium

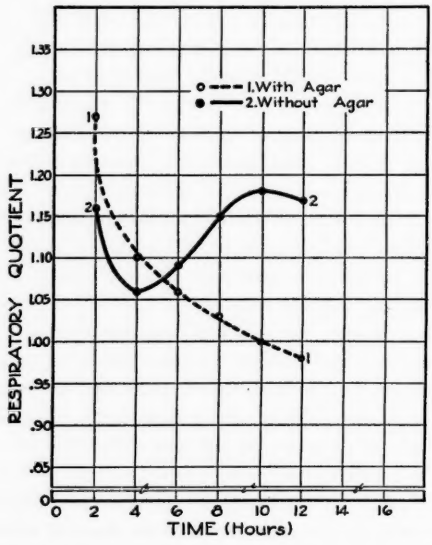

FIG. 2. THE RESPIRATORY QUOTIENTS OF RHIZOBIUM MELILOTI FOR CONSECUTIVE 2-HOUR INTERVALS WHILE GROWING IN A GLUCOSE-NITRATE MEDIUM WITH AND WITHOUT AGAR PRESENT

Inoculum freed of accessory growth substances by culturing in KNO_3-cane sugar medium

DISCUSSION

In a previous investigation concerning accessory growth factors for the rhizobia (7) a similarity was found between the stimulative effects of such materials as alcoholic extracts of cane sugar and brown cane sugar and the effects of reducing agents such as cysteine and thioglycollic acid. The data presented in the present paper show that the substances which were able to stimulate the growth and respiration of the rhizobia also brought about a decrease in the respiratory quotients of the organisms. The period of time during which the respiratory quotients of any culture was depressed varied with the different substances employed. Soil extract, *Az. vinelandii* medium extract, brown cane sugar, and cysteine, usually brought about a decrease in the quotients for only the first few hours subsequent to inoculation. With such materials as yeast and legume extracts the respiratory quotients were depressed over a much longer period of time. The important effect appeared to be the initial lowering of the quotient. Thus, yeast extract and brown cane sugar, in many cases, exerted about equal stimulative effects upon the oxygen consumption of the organisms. Brown cane sugar brought about a decrease in the respiratory quotient for only a very few hours, however, whereas yeast extract had a similar effect throughout most of the growth period of the organisms. These results seem to warrant the conclusion that the growth of the rhizobia in a new medium is greatly favored by the presence of an initial hydrogen donator or a reducing agent. The work of Allyn and Baldwin (3, 4) indicates that the function of such materials might be either to establish, or to aid the organisms in bringing about, a potential of the medium favorable to their growth.

The fact that cysteine was not able to induce as rapid growth and oxygen utilization of the organisms in the media composed of purified materials as were many of the other substances studied, suggests that the beneficial effects of these substances might not be restricted to the creation of a more favorable potential in the medium. It is not improbable, however, that the reducing effects of such materials as soil extract and brown cane sugar can not be simulated by such a drastic reducing agent as cysteine, even in very low concentrations.

It seems likely that the lowering of the respiratory quotients was a result of a direct physiological effect upon the organisms. The effect is most readily explained by the hypothesis that the various materials which brought about the lowering of the quotients acted as hydrogen donators to the organisms. Such substances as soil extract and brown cane sugar, which affected the respiratory quotients for only short periods of time, therefore, might be designated as "initial hydrogen donators." It appears probable that the presence of readily available initial hydrogen donators in the media would benefit the organisms, not only by enabling them to lower the potential of the medium to a more favorable point, but also by furnishing them a very available initial source of energy. This would enable the organisms to make the various adjustments

which seem to be necessary when bacteria are inoculated into a new medium. Such a theory is supported by the observation that the various materials, though furnishing almost negligible additions to the total energy supply of the media, brought about considerable decreases in the lengths of the lag periods of the organisms.

SUMMARY

The physiological effects of various materials upon *Rh. trifolii* and *Rh. meliloti* were studied by the measurement of oxygen consumption and CO_2 production in Warburg manometers.

Brown cane sugar, soil extract, *Az. vinelandii* medium extract, and cysteine added to KNO_3 or NH_4Cl media brought about a decrease in the respiratory quotient of *Rh. trifolii* for the first few hours after inoculation.

Yeast and alfalfa extracts lowered the respiratory quotient of *Rh. trifolii* throughout most of the period of active growth.

Agar brought about a lowering of the respiratory quotient of *Rh. meliloti* in a glucose-nitrate medium but not in a glucose-yeast extract medium.

Attempts to measure the oxidation-reduction potential of different media with an electron tube potentiometer were not very satisfactory. Indications were obtained, however, that the accessory growth substances studied reduce the oxidation-reduction potential of KNO_3-sucrose c.p. media.

One of the important functions of accessory growth substances for Rhizobium seems to be to provide an initial hydrogen donator. The rôle of a hydrogen donator for the nodule bacteria appears to be at least two-fold: first, it tends to lower the oxidation-reduction potential of the medium, and, second, it furnishes the organisms with a readily available initial source of energy which enables them to make the necessary adjustments for the establishment of favorable growth conditions.

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BOOK REVIEWS

Wild Flowers. By HOMER D. HOUSE. The Macmillan Company, New York, 1935. Second Printing. Pp. 362, figs. 35, full color illustrations 264.

The purpose of the author in preparing this attractive volume is indicated as follows: "The present volume is offered, with its wealth of color and form, scarcely approaching the beauty of the growing and living plants depicted, with the hope that the interest which it may stimulate in our native and naturalized wild flowers will become a potent force for their preservation and protection."

The work is particularly timely because of the rapidly growing interest among thinking people in our forests, prairies, parks, and arboreta. It is a part of the great conservation movement to which the Nation is committed. The author has rendered a distinct service to the large public interest in the conservation of wild life.

The book is well arranged and beautifully illustrated in color. It will bring much profit and pleasure to the student and to the general reader and should find a place on the shelves of our libraries.

Ferns of the Vicinity of New York. By JOHN KUNKEL SMALL. The Science Press, Lancaster, Pa., 1935. Pp. 285, map 1, illus. 85.

Lovers of this important group of our plant kingdom will find much satisfaction and pleasure in reading this book. The contents of the volume are best indicated by the following list of topics: Fern family—Polypodiaceae; Curly-grass family—Schizaeaceae; Cinnamon-fern family—Osmundaceae; Adder's-tongue family—Ophioglossaceae; Pepperwort family—Marsileaceae; Salvinia family—Salviniaceae; Horsetail family—Equisetaceae; Clubmoss family—Lycopodiaceae; Spikemoss family—Selaginellaceae; Quillwort family—Isoetaceae. Aside from these, the treatise contains a preface, introduction, map, taxonomic list with citations, comparative lists, authorities cited in this work, glossary, and index.

The author notes that "The amateur botanists of Manhattan and vicinity were the first on the Atlantic seaboard to organize themselves into an association—The Torrey Botanical Club—for the study of plants from a botanical standpoint, growing naturally within a certain region, in this case an area two hundred miles in diameter with Manhattan Island at the center was designated. This region has come to be known as the Local Flora Area." The author notes further that "The preparation of this work was prompted by the lack of a book devoted to the ferns of the Local Flora Area. It is based mainly on collections of ferns preserved in the herbarium of The New York Botanical Garden, besides studies in the field, both within and without the Local Flora Area."

The value of the book is materially increased by the numerous fine illustrations.

The Mushroom Handbook. By LOUIS C. C. KRIEGER. The Macmillan Company, New York, 1936. Pp. xiv + 538, figs. 126, colored plates 32. Price $3.50.

Commercial mushroom growing has already attained a rather definite place in our agricultural economy. The present work, with its beautiful illustrations and clear descriptions, is a distinct contribution to the subject. To quote the author: "In recent years considerable interest in mushrooms has become manifest. Even clubs for their study, so-called mycological clubs, have been formed in various parts of the country, particularly in the large cities. The Federal and most State governments have issued literature advising which kinds to eat and which to avoid. New York State may be said to have done not only pioneer but effective work in the accumulation and dissemination of knowledge concerning mushrooms." The author says, further: "It is not surprising that the public is interested in mushrooms. Several reasons exist. First and foremost, many are good to eat, as everyone knows who consults the bills-of-fare of the better restaurants. Some people, especially our Italian and Bohemian fellow-citizens, search woods and meadows for the spontaneous crop that is to be had for little more than the effort required in the picking. True, there are poisonous, even deadly kinds, but these one can learn to avoid by acquiring a little knowledge such as this book is intended to convey."

Aside from the list of illustrations, introduction and acknowledgments, and abbreviations, the topics dealt with are as follows: Field Study of Mushrooms and Other Fungi; Conditions Under Which Mushrooms Grow and Thrive; Forest Types, with Reference to Distribution of the Higher Fungi; How to Collect, Study, and Prepare Mushrooms for the Herbarium; Life History and General Characteristics of Mushrooms; Economic Importance of Fungi; Common Edible Mushrooms; Growing Mushrooms; Poisonous Mushrooms; The Wood-Destroying Fungi; The Literature on Mushrooms and Their Allies; and Systematic Account of Selected Larger Fungi. Names of the principal authors of fungus species; a bibliography, a glossary of technical terms, and an index are also given.

The mushroom grower and the general reader will readily acknowledge a debt to the author for having produced an interesting and readable book.

Soils—Their Origin, Constitution and Classification. An Introduction to Pedology. Second Edition. By GILBERT WOODING ROBINSON. Thomas Murby & Co., London, 1936. Pp. xvii + 442, figs. 17, plates 5, tables 44.

This is the revised issue of the first edition, which appeared in 1932. As an admirer of the late Dr. Marbut, the author inscribed the book "In Honour of Curtis Fletcher Marbut."

In the preface to the second edition, the author says:

In presenting the second edition of "Soils," I feel that some indication should be given of the changes which have been made from the original edition, and of the principles which I have followed in making such changes.

In the first place, I have made many small variations from the first edition by correcting erroneous or misleading statements and by clarifying obscure explanations. It is, perhaps, too much to hope that those parts of the first edition which survive have been completely purged of faults. Secondly, I have added some material which, although not modifying the original account, may augment its "corroborative detail." Here it has been necessary to exercise a certain economy in view of the abundance of material available. Thirdly, I have re-cast those portions of the book which appeared to require amendment in view of recent advances. These changes are mainly in the chapters on the Pedogenic Processes, on the Clay Complex, on Base Exchange, on Soil Moisture and on Soil Classification. Fourthly, I have added additional examples in the chapters on the Soil Groups and have somewhat amplified the chapter on Soil Geography. Lastly, I have withdrawn the appendix on Methods of Analysis in view of the publication of Mr. C. H. Wright's book on the subject. The narrative has been increased by 63 pages. When allowance is made for excisions and replacements, it will be seen that the amount of fresh material is considerable. About 150 new bibliographical references have been added.

The contents of the book include: preface to first edition; preface to second edition; contents; list of illustrations; and nineteen chapters designated as follows: Introductory; General View of the Constitution of the Soil; The Pedogenic Processes; The Clay Complex; Base Exchange and other Reactions of the Colloidal Complex; Soil Organic Matter; General Physical Properties of Soils; Water Relationships of Soils; Soils of the Podsolic Group; Tshernosems and their Related Groups; Ground-water Soils—Including Peats; Saline, Alkaline, and Soloti Soils; Soils of the Humid Tropics and Sub-tropics; Soils Associated with Calcareous Parent Materials; The Classification of Soils; The Geography of Soils; Soil Surveys; Soil Analysis; and Soils, Plant Growth, and Agriculture. In addition to these, there are an index of places and a subject index. The subject matter is well arranged and effectively presented.

Pedology. By JACOB S. JOFFE. Rutgers University Press, New Brunswick, New Jersey, 1936. Pp. xvi + 575, plates 41, figs. 4, tables 136.

A satisfactory definition of the term *pedology* is supplied by the author in his foreword:

Pedology is the science of soils. Its scope is the study of the phenomena presented to us by the soil body in its natural position. Pedology is thus that realm of natural science which has as its objective the elucidation of the natural laws governing the origin, formation, and distribution of soils. Pedology should not be confused with soil science, which is a broader subject, embracing pedology and its applied phases such as agronomy, soil fertility, soil reclamation, soil physics, soil chemistry, and soil biology or rather the physics, chemistry, and biology of soils. Although pedology is not a fundamental science as is physics, chemistry, or mathematics, it is an independent science dealing with a natural body, the soil, just as botany is an independent science dealing with a natural body, the plant, or zoology dealing with a natural body, the animal.

The treatment as developed by the author rests on the broad generalization laid down by the Russian School of Soil Investigators. The late Curtis F.

Marbut, of the United States Department of Agriculture, offers a clear explanation of the significance of the contributions made by the Russian School of Pedologists. In his introduction to Dr. Joffe's book he says:

> At the time when western Europe was still engaged in the futile assertion that the soil as soil is dominated in its general features by the materials out of which it has been built, the Russian workers had already shown that the soil is the product of process rather than of material and is, therefore, a developing body rather than a static body. They allied the soil to life rather than to death.
>
> Fortunate in the mid-continental location of the country in which they worked, equally fortunate in its broad geographic extent, the relatively slight extent to which man had interfered with the normal course of Nature's processes and the clearness with which the results of her processes in soil development are expressed, the Russian workers were able to see, with remarkable clearness, relationships that in western Europe are either obscurely expressed or not expressed at all.
>
> In the clearness and simplicity with which the great soil features, as well as their relation to environment, are expressed, Russia occupies a place in the development of pedology comparable to that of the western United States in the development of the science of land form development. Whether our Russian colleagues are to be praised or merely congratulated may be a debatable question, but that the fundamental principles of the science of the soil were first laid down by them on the basis of conditions and facts in their own tremendously varied country is not debatable. Dokuchaev and his co-workers occupy the same position in pedology as do Sir Charles Lyell and his co-workers in geology, and Linnaeus in botany.

Aside from the frontispiece, the foreword by the author, and the introduction by Dr. Marbut, the book is made up of two parts—Soil Genesis and Soil Systematics—, and appendices. Part I contains six chapters, entitled, respectively: Pedology as a Scientific Discipline; Soil as a Natural Body; Soil Defined, Soil Morphology and Methods of Studying it; Soil Genesis: Weathering and Soil Formation; Soil Genesis: Soil Formers; and Soil Genesis: Soil Forming Processes. Part II contains ten chapters which are entitled, respectively: Desert, Semi-Desert, and Arid Steppe Types of Soil Formation: Gray, Brown, and Chestnut Brown Soil Zones; Chernozem Type of Soil Formation; Podzol Type of Soil Formation; Subtypes and Transition Types of Soils in the Podzol Zone; Tundra Type of Soil Formation; Laterites and Lateritic Type of Soil Formation; Intrazonal Soils: Solonchak, Solonetz, Solodi, Rendzina, etc.; Bog and Marsh Soils; Mountain Soils; and Some Pedological Features of the Soils of the United States. A selected list of books and monographs on soils with special reference to pedology is also supplied. The index of authors and also the index of subjects are helpfully arranged.

The present volume will render a wide and useful service, particularly in view of the growing interest in soil conservation, the relation of soil environment to land use, and the state, regional, and national policies centering around methods of soil management and guided by the recent as well as older information that has been gained by soil technologists in this and other countries.

Les Sols de France au Point de Vue Pédologique. By V. AGAFONOFF with introductory statements by M. A. LACROIX, M. L. LUTAUD, AND M. A. DEMOLON. Dunod, Paris, 1936. Pp. xiii + 154, maps 2, tables 23, figs. 23.

The author obtained his early training and experience in Russia. He has prepared his treatise on the basis of the methods of soil classification developed by the Russian pedologists. The work is an important contribution to the mapping and classifications of the soils of France. The importance attached to the work by Dr. Agafonoff's colleagues is indicated in their introductory statements. The following quotations are, in the order given, from the statements of Lacroix, Lutaud, and Demolon.

> The scientific study of the soil is his passion. Familiar with the methods of the Russian School of Pedologists, he has made it his task, first of all, to make these familiar and appreciated in France—not under the form of a theoretical exposition, but by employing a more personal procedure, which consists in undertaking a study of our own soils from a point of view quite different from what has been considered until the present time.
>
> . . . . . For the first time the methods and results of the Russian School of Pedologists have been applied to our own country by a prominent investigator, who has not hesitated during the last few years to undertake a systematic study of our different provinces, to observe the soil directly, to collect personally, with methodical care, samples necessary for this study. This work appears now as the result of personal, patient and careful efforts. This is a new book for us and, what is more important, it opens a new point of view. All those who read it will recognize the interest and talent with which the author has conducted and achieved his task.
>
> . . . . . With admirable perseverence, M. V. Agafonoff has applied during many years to the soils of France the principles of those that laid the foundation of pedology—Dokoutchaïev, Sibirtzev and Glinka. The importance of climate and vegetation in the origin and evolution of soils represents a great idea, which has taken the place of the previous insufficiently comprehensive conceptions of the true nature of the soil. In this new conception biology now plays a very important part. In a parallel manner, the methods of examination of the soil were modified and the consideration of the profile enlarged the field of exploration. which was too limited at the surface. It is not exaggeration to say that a study of the soil has brought about during recent years a complete rejuvenation and a new orientation. We are indebted to M. V. Agafonoff, who has contributed largely, by his pedological studies, to the soils of France.

The four chapters of the book are entitled, respectively: Pedology—A New Science; The Research Plan and Our Methods for the Examination of the Soils of France; Soil Regions of France; and Azonal Soils.

Soil Science—Its Principles and Practice. By WILBERT W. WEIR. J. B. Lippincott Company, Chicago—Philadelphia, 1936. Pp. vii + 615, figs. 134.

The title "Soil Science" has apparently not been used previously for the designation of textbooks dealing with soils, soil fertility, and fertilizers. The term has been used for the designation of the international journal SOIL SCIENCE, established by the reviewer in 1915. It was the author's intention to present the subject in its broad relations, even though he has stressed the applied phases of soil science.

The opening paragraph in the author's preface reads as follows:

> Possibly there is no subject that lies closer to the welfare of the human race, with its population of nineteen hundred millions of people, than the production and maintenance of

the necessary food supply; and it is particularly gratifying to know that today soil science has so far advanced that one may confidently assert that, in the absence of some catastrophe of nature or a war of extinction, mankind need never fear starvation or the want of food. Such an eventuality has been made unlikely by scientific methods of agriculture, increased knowledge of the soils themselves, better understanding of plant growth, and improved methods for taking care of and preserving the soils.

A further examination of the contents of the book shows it to embrace 27 chapters and an index. The several chapters are designated as follows: Development of Agriculture and Rise of Scientific Thought; Physical Constitution of Soils; Physical Properties of Soils; Chemical Nature of Soils; Microbial Population of Soils; The Modern Concept of Soils; Soil Classification; Natural Order in Soils; Soil and Plant Relationships; Crop Production and Soil Fertility; Tilth and Tillage; Soil Water and Soil Fertility; Irrigation and Land Drainage; Aëration as a Factor in Soil Fertility; Soil Reaction and Soil Fertility; Soil Acidity and Soil Alkalinity; Science and Art of Liming Acid Soils; Organic Matter and Soil Fertility; Micro-organisms and Soil Fertility; Plant Nutrient Elements; Fertilizers; Fertilizers, Their Effects on Soils and Plants; Fertilizing Plants to Meet Their Nutrient Requirements; Crop Rotation and Soil Fertility; Soil Erosion; Determining the Need for Fertilizers; and Interpreting Results of Fertilizer Experiments.

The reader's attention may be directed particularly to the fact that the author has made himself thoroughly familiar with soil research at the American agricultural experiment stations and has presented some of their important findings in a readable and logical form.

Problems in Soil Microbiology. By D. W. CUTLER AND L. M. CRUMP. Longmans, Green and Co., London—New York—Toronto, 1935. Pp. vii + 104, figs. 18, tables 32, maps 1. Price $3.20.

The authors note in the preface:

This book incorporates the substance of a series of lectures delivered by one of us (D. W. C.) at the University College of Wales, Aberystwyth, on the Aberystwyth Lecture Foundation during the session 1934–35. The contents are largely the result of work carried out in the General Microbiology Department of the Rothamsted Experimental Station by the authors and their colleagues, and it is in no sense a textbook of soil microbiology.

The theme throughout is to show that from the biologist's viewpoint the soil is an eminently suitable home for living organisms and that, through the long ages of evolution, a population has been selected which is, on the whole, so unspecialized that almost any substance which finds its way into the soil, either naturally or in the course of modern agricultural practice, will eventually become incorporated into the general soil economy.

The contents of this interesting book are indicated in the titles of the seven chapters, which are as follows: The Suitability of the Soil for Micro-organisms; The Bacterial Population under Field Conditions; The Relation of Bacteria to Nitrite; Carbon Dioxide Production by Soil; The Growth of Protozoa in Pure Culture; The Behaviour of Protozoa in Soil; and The Inter-Actions between

the Soil Organisms. The authors have also provided a bibliography, an index, and a map of protozoan distribution.

The History of the Upper Mississippi River in Late Wisconsin and Postglacial Time. By WILLIAM S. COOPER. The University of Minnesota Press, Minneapolis, Minn., 1935. Pp. xii + 116, figs. 46, plates 4. Price $4.00.

The nature of this treatise is indicated in the author's foreword. He says:

> This study in glacial geology is the work of a botanist who is a firm believer in what has been aptly termed "cross-fertilization of the sciences." It developed gradually from a beginning that was purely botanical. An area of ancient dunes close to Minneapolis supports a flora that is distinctive and of unusual interest. An ecological investigation begun here necessitated consideration of the dunes themselves. Steadily the field broadened in the manner familiar to every scientific worker. The dunes led back to their source in the outwash. A great glacial lake disclosed itself. Finally the various elements resolved themselves into a history, in which the Mississippi River plays the leading rôle. Concurrently the botanical field expanded until it covered the vegetation of both dunes and outwash, with particular emphasis upon its development during postglacial time. The foundational geologic study is here presented, the botanical part is still unwritten.

The contents of the treatise consist of: The Field of Inquiry; The Patrician (Middle Wisconsin) Glaciation; The Late Wisconsin Glaciation; Postglacial Entrenchment of the Mississippi and St. Croix Rivers; The Dunes; a bibliography; and an index.

The author has succeeded in telling an interesting story—interesting both as to facts and implications. One senses in reading the book the part that has been played by The Father of Waters in carving the face of North America.

A Provisional Soil Map of East Africa (Kenya, Uganda, Tanganyika, and Zanzibar) with explanatory Memoir. By G. MILNE. East African Agricultural Research Station, Amani—Tanganyika Territory, 1936. Pp. 34. Price 5/— post free.

The soil technologist may, with propriety, apply a trite saying to his field of study—"the world is growing smaller" in respect to soil classification and mapping. Much has been added within the past five years to our inventory of the soil resources of the world. Notable contributions were made in this field by the Third International Congress of Soil Science, which was held at Oxford, England, in 1935. Some of the data appearing in the present memoir were presented at that Congress. The students of soils will note that the map in question includes Kenya, Uganda, Tanganyika, and Zanzibar. Thus, we are beginning to know more about the soil resources of a continent where human civilization saw its early beginnings.

The memoir is made up of two parts entitled General Description, and the Soils of the Four Dependencies. The specific topics dealt with in these parts and the names of the contributors to the second part are given below: Part I: General Description—Aims, Origin, and Authorship; Area Included, Outline,

and Scale; Sources of Information; Classification of Soil Types,—Table of Soil Groups, Desert Soils, Saline Soils, Plains Soils, Black or Grey Clays, Mottled Clays, Red Earths (two groups), Plateau Soils, Podsolised Soils, and Lithological Types; Colouring and Notation; Occurrence of Soil Types in Association,—The Catena, Other Complex; and General Conclusions. Part II: The Soils of the Four Dependencies: Kenya Colony and Protectorate (V. A. Beckley and G. H. Gethin Jones); The Uganda Protectorate (W. S. Martin and G. Griffith); Tanganyika Territory (G. Milne); and the Zanzibar Protectorate (L. W. Raymond).

The soils described in this volume are interesting from many points of view. The authors have done pioneering work and have carried on their tasks even under trying and difficult circumstances. Their contribution gains in value because of the circumstances under which their work was performed.

Die Lage der Landwirtschaft im Freistaat Sachsen—Heft 3. By WOLFGANG WILMANNS AND HERMANN ISENSEE. Verlag von Theodor Steinkopff, 1936. Pp. vi + 72, illus. 20, maps 2. Price 2.50 RM. (paper cover).

The investigation of agricultural production is one of the major issues of present-day Germany. Hence the description of the status of agriculture in Saxony as given in the present volume should interest agronomists and agricultural economists. The report is made up of two parts dealing respectively with the agricultural conditions in Saxony and the status of production and its effect on the agricultural conditions in the harvest years 1931–1932 and 1932–1933. The general topics discussed in Part I are the General Basis of Agriculture in Saxony and the Status of Progress in Agriculture in the harvest years 1931–1932 and 1932–1933. Part II contains as its major topics General; Methods of Study; and Results. Altogether the report contains much interesting material and would furnish helpful information to the student of European agriculture.

Fertilizer in Crop Rotations—Issue I—A Collection of Papers edited by S. P. KULZHINSKII, A. S. CHERNAVIN, AND S. S. SIGARKIN. Moscow and Leningrad, U. S. S. R., 1934. Pp. 216.

The major topics dealt with in the book are as follows: Under Problem of Studying and Working out a Fertilizer System in Crop Rotations, by S. S. Sigarkin; Agro Technical Principles of Working out a System of Fertilization, by I. V. Yakushkin; Legumes in Crop Rotations as a Factor of the Effectiveness of Fertilizers, by S. P. Kulzhinskii; Manure in Crop Rotations, by B. G. Naidin; Green Manures in Crop Rotations, by E. K. Alekseev; Peat and Peat Fertilizers in Crop Rotations, by B. A. Kabanov; Liming in Crop Rotations, by S. S. Yarusov; Rock Phosphate Flour in Crop Rotations, by S. V. Shcherba; A System of Fertilization and a Study of it in Economies of 100 Percent Chemization Conducted by the Institute of Fertilizers and Agro-Pedology, by A. I. Tutkevich; Fertilizers in Crop Rotations with Flax, by Ya. V. Peive; Fertilizer

Placement in Crop Rotations with Grain, by I. V. Yakushkin; Fundamental Principles in Working Out a System of Fertilization in Sugar Beet Culture, by G. B. Neiman; On the Problem of the Systems of Fertilizers in Vegetable Gardening, by S. T. Antoshin.

The rapid development of agricultural research in the Soviet Union adds interest to the efforts now being made in that country to develop the rational use of agricultural land and the maintenance and improvement of yield levels with the aid of crop rotations and fertilization.

Ergebnisse Der Agrikulturchemie. Part IV, 1935. Edited by F. ALTEN AND M. TRÉNEL. Verlag Chemie, Berlin, 1936. Pp. 229, 87 tables, 40 illus. Price 12 RM.

This is the fourth volume of a series. The present work is a desirable addition to the various reviews on progress in agricultural chemistry. The nature of the data dealt with by the author is clearly noted in the table of contents. Sections A to E are designated respectively: General; Investigation of Soils; Fertilization; Feeding; and Nutrition. A general review supplied by the authors may be noted as follows:

> With the publication of this volume the tradition is continued of annually collecting the important reports from the division of agricultural chemistry of the convention of the Union of German Chemists. The suggestions and scientific points of view given in the reports should reach other scientific groups through this publication. The reports give an excellent idea of the scientific status of agricultural chemistry. They show the important part played by the studies of the agricultural chemists in practical agriculture and at the same time give the scientist a perspective of new chemical problems in production.
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> The "Ergebnisse der Agrikulturchemie" is not only a valuable source of scientific inspiration to the chemist but it is also a practical and indispensable aid to the agricultural advisor and teacher.

The authors and their collaborators have done well in creating a picture of progress in a very important field of agricultural science. Teachers, students, and progressive farmers should add this volume to their collection of reference material.

Colloids in Agriculture. By C. E. MARSHALL. Edward Arnold & Co., London, 1935. Pp. viii + 184, figs. 14, tables 12.

The field of colloidal chemistry has already furnished a vast quantity of data which serve to explain fundamental facts and relations in agricultural production and the utilization of agricultural products. To quote the author's own words: "I have written this book with an eye to the needs of two classes of readers. Firstly, I hope it will prove useful to our county organizers, district lecturers and rural instructors—indeed, to all who are engaged in scientific agriculture and who are interested in the application of our latest knowledge to their field work and their teaching. I have written also for our agricultural students. To them, few subjects are more confusing than colloid chemistry, due largely to our haphazard methods of teaching."

Part I of the book deals with the Realm of Colloids. Respectively, the chapters are designated: The Nature of Colloids; The Formation of Colloids; The Properties of Small Particles in Suspension; The Properties of Molecules at Surfaces; Ions at Surfaces; and Soils and Gels. Part II deals with Colloids in the Soil, and contains the following chapters: The Mineral Colloids of Soil; The Organic Colloids of Soil; Colloids in Soil Formation Processes; and Colloids and Soil Texture. Part III has to do with Colloids in Plant and Animal Life. It contains the following chapters: Some Colloidal Materials Present in Living Organisms; Colloidal Architecture in Biological Structures; Milk and Milk Products as Colloidal Systems; and Smoke Damage and Plant Protection. These are followed by an index.

This book will no doubt be accepted as a welcome addition to the reference shelves of teachers, students, and progressive farmers.

Die Methoden zur Bestimmung des Kali- und Phosphorsäure-Bedarfs landwirtschaftlich genutzter Böden. By WALTER-ULRICH BEHRENS. Verlag Chemie, G. M. B. H., Berlin, 1935. Pp. 196, tables 140.

There is much interest at the present time in the so-called rapid methods for the determination of soil deficiencies in respect to potassium, phosphorus, calcium, and other plant nutrients. The present work deals with the subject from the scientific as well as the technical point of view. As is noted by the author in his preface, "The number of contributions relating to the determination of the plantfood needs of our cultivated soils has become unusually large. I have gone through the material and have brought together the most important results." The author also notes that "A particular effort was made to carry out a critical review of the different methods." In this way, he has rendered a helpful service to many workers in the field.

The major divisions of the book deal with: A—Underlying Principles; B—The Individual Methods of Soil Investigation in Respect to the Requirements of Potash and Phosphoric Acid; and C—The Technique of Sampling and of Analysis. There are a bibliography of 13 pages and author and subject indexes.

Arbeiten über Kalidüngung. Vol. II. By O. ECKSTEIN. Verlagsgesellschaft für Ackerbau M. B. H., Berlin, 1935. Pp. 478, illus. 123, tables 198.

Volume I of this treatise was reviewed in the June, 1932, issue of SOIL SCIENCE.

Summaries of the four major divisions of the book are given in English. The titles of these divisions are: Soil Research; Physiological Investigations; Investigations on the Influence of Commercial Fertilizers on the Chemical Composition and Nutritional Value of Food and Feeding Stuffs; and List of Papers Published by the Experiment Station, Berlin-Lichterfelde. There is also a subject index.

To quote from the preface in English as given by the author:

In nearly every country to-day there is a general opinion that agriculture can only be made to pay by the intensive use of all auxiliary methods which science can place at the disposal of the practical farmer. In countries where the area of cultivated land is relatively small, the realisation of the above point is shown by the fact that every possible acre is raised to the highest degree of productivity by the use of the best pedigree seeds or plants, thorough cultivation, careful regard to drainage and by the judicious and liberal use of commercial fertilisers. . . . As has already been pointed out, agricultural problems, and especially the handling of soil questions, are fundamentally dependent upon local agricultural conditions. It is of special interest in this respect to compare conditions in different countries, e.g. in the United States of America with those in Germany. The function of the German farmer is to secure as large yields as possible, consistent with suitable quality, and especially maximum yields of crops rich in protein, fat and fibers respectively. In the United States of America, however, where agricultural over production during recent years has been an economic calamity, the problem is quite a different one. In most oversea countries the problem is to raise the quality of the crops, so far as quality influences the capacity of the market to absorb them, to as high a degree as possible and to promote the culture only on the most suitable soils and by the best possible crop treatment.

There are a bibliography of 47 numbers and a subject index.

JACOB G. LIPMAN.